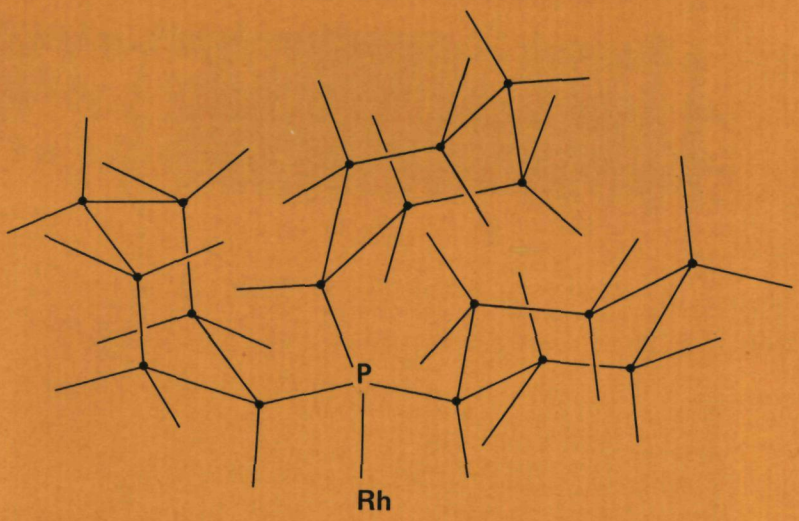
TRICYCLOHEXYLPHOSPHINE–RHODIUM COMPLEXES AND ASPECTS OF π–ACID COORDINATION



H.L.M. van Gaal

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PROMOTOR : PROF.DR.IR. J.J. STEGGERDA

CO-REFERENT: DR. A. VAN DER ENT

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P R O E F S C H R I F T

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE WISKUNDE EN NATUURWETENSCHAPPEN AAN DE KATHOLIEKE UNIVERSITEIT TE NIJMEGEN, OP GEZAG VAN DE RECTOR MAGNIFICUS PROF.DR. A.J.H. VENDRIK VOLGENS HET BESLUIT VAN HET COLLEGE VAN DECANEN IN HET OPENBAAR TE VERDEDIGEN OP VRIJDAG 25 FEBRUARI 1977 DES NAMIDDAGS TE 2 UUR PRECIES

door

HENRICUS LAMBERTUS MARIA VAN GAAL
geboren te Schaijk

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La critique est aisée,
l'art est difficile

C O N T E N T S

CHAPTER I

GENERAL INTRODUCTION

CATALYSIS AND COORDINATION NUMBER

The interest in phosphine complexes of the group VIII metals arises from their usefulness as homogeneous catalysts and stoichiometric reagents in organic syntheses, such as the hydrogenation, hydrohalogenation, hydrosilylation, hydroformylation, oxidation, isomerization and polymerization of unsaturated compounds[1-4]. An interesting point is that one transition metal compound may catalyse a large range of organic reactions. Compounds derived from rhodium(I)-phosphine complexes are such versatile catalysts, the proto-type being $RhCl(PPh_3)_3$, discovered in 1965 by Bennet *et al.*[5] and Osborn *et al.*[6].

As an example of a catalytic cycle and of counting coordination numbers and metal valence electrons[7], we give a simplified description of the hydrogenation of an alkene by $RhCl(PPh_3)_3$[6,7] (Fig. 1).

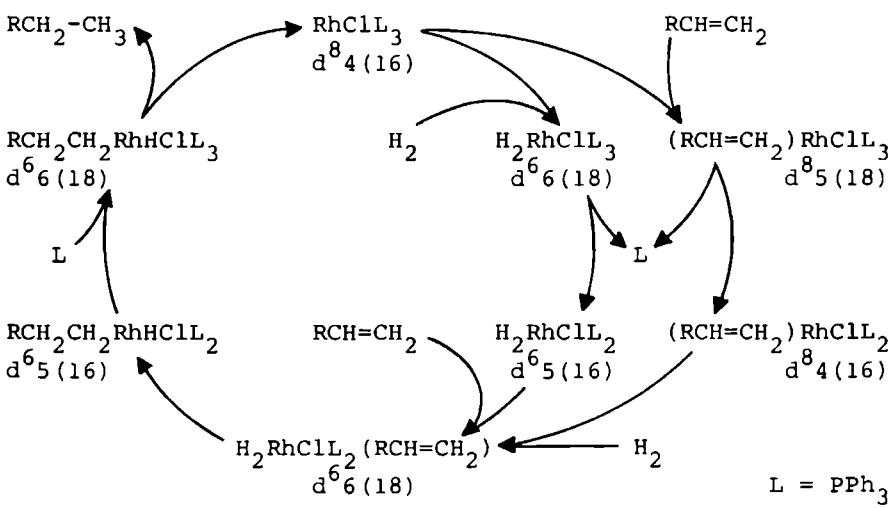

Fig. 1: Hydrogenation with $RhCl(PPh_3)_3$

In this cycle, the metal centre seems always to have a 16 or 18 electron configuration. The departing triphenylphosphine, however, does not have a well-established role in this cycle, and other intermediates may be present. In fact, the occurrence of a three-coordinate species $RhCl(PPh_3)_2$ has been postulated, but never been proven[6,8]. In nickel, palladium and platinum chemistry, 14 electron M(0)-d^{10} compounds have been isolated (notably, but not only, with PCy_3: $M(PCy_3)_2$, M = Ni[9], Pd[10] and Pt[11]), but in cobalt, rhodium and iridium chemistry, no definitive evidence for a three-coordinate 14-electron species has been given.

During the catalytic process one or more of the reactants are temporarily coordinated to the metal centre. This may be the coordination of an unsaturated molecule to the metal, in which the formal oxidation state of the metal is retained, or the oxidative addition of a reactant such as molecular hydrogen, in which the rhodium formally changes from the oxidation state +I to +III. Although paramagnetic rhodium(II) complexes have also been detected in catalytic systems, it has been found in some cases that they do not take part in the catalytic cycle.

In order to be able to add the incoming reactants, the metal needs in an intermediate stage a vacant coordination site. The metal is then called coordinatively unsaturated. Coordinative unsaturation is "perhaps the single most important property of a homogeneous catalyst"[12]. It is defined with respect to the coordinatively saturated state in which the metal has a closed shell noble gas configuration with 18 valence electrons[7]. The study of coordinatively unsaturated complexes, models for intermediates in catalytic processes, is greatly facilitated by the presence of bulky ligands, as these may stabilise the unsaturation by shielding of the metal centre. Tricyclohexylphosphine is the bulky ligand we use in this thesis.

The most common valencies for rhodium and its chemically nearest, iridium, are +I and +III. Coordinatively un-

saturated five-coordinate rhodium(III) and iridium(III) d^6 systems are mostly less stable than the corresponding six-coordinate Rh(III) and Ir(III) systems. In contrast, for Rh(I) and Ir(I) d^8 systems "the criteria for relative stability of 5- and 4-coordinate species are by no meens fully established"[13]: often the coordinatively unsaturated four-coordination prevails, but in the presence of strongly electron-withdrawing ligands five-coordination seems to be more readily realised[14].

TRANSITION METAL ACID-BASE BEHAVIOUR AND π-ACID LIGANDS

Lewis acidity is caused by the presence of relatively low-lying empty orbitals, and is therefore related to the electron affinity of the species: basicity, in turn, is caused by the presence of relatively high-lying filled orbitals, and is related to the ionisation potential. When both types of orbitals are present, with only a small energy difference between them, the species (whether ligand or metal) is called "amphoteric"[15] or "biphilic"[14]. A Lewis base is also called a donor or nucleophile, and a Lewis acid also an acceptor or electrophile.

As most classical ligands are Lewis bases, transition metals have normally been considered acids. In the last decade, the potential basicity of low-valent transition metals has been recognised[16]. In fact, the transition metal is biphilic in two senses: (i) in the same complex it may be an acceptor for some ligands and a donor for others, and (ii) towards a biphilic ligand, the metal may act simultaneously as acceptor and as donor. In the latter case, the donor-acceptor interactions are classified according to the local symmetry of the orbitals in the metal-ligand fragment[17,18]. In most cases the ligand is a σ-donor; in its π-interactions with the metal it may either be a donor or an acceptor. A ligand with π-accepting properties is commonly called a π-acid. Examples of π-acids are carbon monoxide

and molecular nitrogen, which are mostly end-on or mono-hapto (h^1) coordinated, and ethene, acetylene and dioxygen, which are mostly side-on or di-hapto (h^2) coordinated.

The relative and absolute importance of donor and acceptor interactions between a metal and its ligand is a subject of continuing discussion.

TRICYCLOHEXYLPHOSPHINE AS A LIGAND

For a discussion of the properties of PCy_3 it best can be compared with other phosphines and phosphites. In Table 1 some data are collected on electronic, steric and kinetic data of several of the more bulky phosphorous ligands.

T A B L E 1

SOME PROPERTIES OF MORE BULKY PHOSPHINES, PHOSPHITES AND COMPLEXES THEREOF

Ligand L	ν(CO), cm^{-1} of $Ni(CO)_3L$, A_1 mode[19]	minimum cone angle[20]	rate constant, $mol^{-1}sec^{-1}$ $Rh(C_5H_5)(CO)_2 + L \rightarrow Rh(C_5H_5)(CO)L + CO$[21]
$P(t\text{-}Bu)_3$	2056.1	182± 2	
PCy_3[a]	2056.4	179±10	7.7×10^{-5}
$P(i\text{-}Pr)_3$	2059.2	160±10	
$P(n\text{-}Bu)_3$	2060.3	130± 4	3.3×10^{-3}
$P(o\text{-}Tol)_3$	2066.6	194± 6	
PPh_3[a]	2068.9	145± 2	2.9×10^{-4}
$P(O\text{-}o\text{-}Tol)_3$	2084.1	165±10	
$P(OPh)_3$	2085.3	121±10	7.3×10^{-5}

a) the pK_a of $HPCy_3^+$ is 9.70 and of $HPPh_3^+$ 2.73 (ref. 22)

T A B L E 2

LITERATURE SURVEY OF RHODIUM AND IRIDIUM TRICYCLOHEXYL-PHOSPHINE CHEMISTRY. L = PCy_3

Compound	Preparation	Ref.
Neutral M(I) d^8		
$RhX(CO)L_2$	$[RhX(CO)_2]_2$ + 2 L (X = Cl, Br), $RhX(CO)(PPh_3)_2$ + 10 L	28,29
$RhX(CO)(PPh_3)L$	$RhX(CO)L_2$ + 10 PPh_3 (X = Cl, Br)	29,30
$RhI(CO)(PPh_3)L$	$RhI(CO)(PPh_3)_2$ + 10 L	29
$RhCl(CO)[P(OPh)_3]L$	$RhCl(CO)L_2$ + 10 $P(OPh)_3$	29
$Rh(NCS)(CO)L_2$	$RhCl(CO)L_2$ + 4 KSCN	31
$Rh(BH_4)(CO)L_2$	$RhCl(CO)L_2$ + $NaBH_4$	32
$Rh(C_5H_5)(CO)L$	$Rh(C_5H_5)(CO)_2$ + L (not isolated)	33
$IrCl(CO)L_2$	$[IrCl(CO)_3]_n$ or $[IrCl_2(CO)_2]^-$ + n L	34
$IrBr(CO)L_2$	$[IrBr_2(CO)_2]^-$ + 2 L	35
$IrI(CO)L_2$	$IrCl(CO)L_2$ + 100 NaI	35
$IrCl(CO)[P(OPh)_3]L$	$IrCl(CO)[P(OPh)_3]_2$ + 10 L	29
$IrCl(CS)L_2$	$IrCl(CS)(PPh_3)_2$ + excess L	36
$Ir(BH_4)(CO)L_2$	$IrCl(CO)L_2$ + $NaBH_4$	32
$Ir(NCBH_3)(CO)L_2$	$IrCl(CO)L_2$ + $NaNCBH_3$	32
$[Ir(SR)(CO)_2L]_2$	$[Ir(SR)(CO)_2]_2$ + excess L	42
$IrCl(CO)L_2(O_2)$	$IrCl(CO)L_2$ + O_2 (not isolated)	23
Cationic M(I) d^8		
$[Rh(CO)_2L_2]^+$	$RhCl(CO)L_2$ + $AlCl_3$ + CO	37
$[Ir(CO)_nL_2]^+$	$IrCl(CO)L_2$ + $AlCl_3$ + CO	37
(n = 2, 3)	or $IrCl(CO)L_2$ + $NaClO_4$ + CO	38,39
$[Ir(CO)_2L_2A]^+$	$[Ir(CO)_2L_2]^+$ + A (A = dimethyl-acetylenedicarboxylate)	38
$[Ir(CO)_2(CS)L_2]^+$	$IrCl(CS)L_2$ + $NaClO_4$ + CO	36
$[IrCl(NO)(CY)L_2]^+$	$IrCl(CY)L_2$ + $NOBF_4$ (Y = O, S)	36

Compound	Preparation	Ref.
Neutral M(II) d^7		
$RhCl_2L_2$	$RhCl_3.3H_2O$ + excess L	26
$RhBr_2L_2$	$RhBr_3.3H_2O$ + excess L	26
Neutral M(III) d^6		
"$RhCl_3L_3$"	$RhCl_3.3H_2O$ + 3 L (doubtful)	25
$[RhCl_3L_2]_n$	"$RhCl_3L_3$" in air (no supporting data)	25
$RhCl_3(CO)L_2$	"$RhCl_3L_3$" or $[RhCl_3L_2]_n$ + CO + Cl_2	25
$RhHCl_2(CO)L_2$	$RhHCl_2L_2$ + CO (procedure reported, but neither starting material nor product described)	25
$RhHCl(C\frown N)L_2$*	$[RhCl(C_8H_{14})_2]_2$ + 4 L + 2 HC$\frown$N	41
$IrHX_2L_2$	K_2IrX_6 + excess L (X = Cl, Br) (not yet fully characterised)	26
$IrHCl_2L_2(py)$	$IrHCl_2L_2$ + pyridine	26
$IrHCl_2(CO)L_2$	$IrCl(CO)L_2$ + HCl	26
$IrH_2X(CO)L_2$	$IrX(CO)L_2$ + H_2 (X = Cl, Br, I) (not isolated)	40
$IrHCl(C\frown N)L_2$*	$[IrCl(C_8H_{14})_2]_2$ + 4 L + HC$\frown$N	41
Cationic M(III) d^6		
$[IrH_2(CO)(CY)L_2]^+$	$[Ir(CO)(CY)L_2]^+$ + H_2 (Y = O, S)	38,36
$[IrCl_2(CO)_2L_2]^+$	$[Ir(CO)_2L_2]^+$ + Cl_2	39

* C$\frown$N = metallated aromatic or olefinic N-base

The relative ligand basicity of a series of ligands may be conveniently studied by comparison of the CO stretching frequency in a series of isostructural carbonyl-containing compounds. Tolman[19] has carried out such an investigation for 70 phosphines and phosphites on the compounds $Ni(CO)_3(L)$. From this, PCy_3 is recognised as one of the most basic phosphines.

PCy_3, along with $P(t\text{-Bu})_3$ and $P(o\text{-Tolyl})_3$, is one of the most bulky phosphines used in coordination chemistry. Tolman[20] calculated from steric models a minimum cone angle under which the phosphine is seen from the metal centre. For PCy_3 this cone angle is found to be $179\pm10^{\circ}$. This implies that PCy_3 exerts some influence on even small ligands *cis* to it, which in fact has been found in a crystallographic study of $NiCl_2(PCy_3)_2$[24]. However, as PCy_3 does not represent a closed cone, other ligands may become situated between two cyclohexyl rings, reducing the cone angle to a smaller effective value[11]. Nonetheless, we expect that more than two PCy_3 ligands can rarely be coordinated to the same metal centre. The report of the *tris*-complex $RhCl_3(PCy_3)_3$[25] has become suspect because of the results of Moers *et al.*, who prepared $RhCl_2(PCy_3)_2$[26] following the reported procedure for $RhCl_3(PCy_3)_3$.

Regarding oxidative addition-reductive elimination processes, PCy_3 complexes show an interesting feature: for 18 electron systems reductive elimination should be favoured on steric grounds, but disfavoured on electronic grounds. These opposing properties of PCy_3 made it a promising ligand for unusual reactions as has been demonstrated by the formation of five-coordinate d^6 $MHCl(CO)(PCy_3)_2$ (M = Ru, Os)[27] and two-coordinate $M(PCy_3)_2$ (M = Ni[9], Pd[10], Pt[11]).

In Table 2 is given a literature survey of rhodium and iridium tricyclohexylphosphine complexes and their preparations. It is noteworthy that all M(I) and nearly all M(III) complexes in this Table contain a carbonyl or a thiocarbonyl ligand, which means that most of the previously pre-

pared rhodium and iridium PCy_3 complexes belong to the more common types of rhodium and iridium phosphine complexes. With the exception of $RhX_2(PCy_3)_2$ (X = Cl, Br)[26], the reported compounds have no particular composition, stability or other properties which depend critically on the bulkiness of the tricyclohexylphosphine ligand.

SURVEY OF THIS THESIS

Exceptional coordination numbers of the rhodium with and without coordinated unsaturated organic molecules, novel modes of coordination of some organic molecules and novel paramagnetic rhodium(II) complexes have been searched by using PCy_3 as a ligand. The bonding between the metal and the organic ligands has been studied by spectroscopic and theoretical methods.

In Chapter II of this thesis, the synthesis and characterisation of three-coordinate species $RhX(PCy_3)_2$ (X = F, Cl, Br, I) and the coordination of unsaturated molecules, including molecular nitrogen, molecular oxygen, acetylenes and heterocumulenes YCZ (Y, Z = S, O, NR) to the three-coordinate complexes are described. Several of the addition complexes have an unusual, low coordination number.

In Chapter III, some oxidation reactions with the complexes $RhX(PCy_3)_2$ are treated. In addition to the preparation of rhodium(III) compounds the synthesis and the E.P.R. spectra of paramagnetic rhodium(II) complexes are described.

In Chapter IV it is shown how the relative donor and acceptor contributions in group VIII metal alkyne complexes may be separated. Infrared intensities are used in addition to the infrared frequencies of the alkyne triple bond stretching vibration, which latter quantity is more commonly used in a qualitative estimate of the metal-alkyne interaction.

In Chapter V, the influence of the coordination geometry on the metal π-backbonding properties is analysed by

orbital correlations and literature data on metal-(π-acid) complexes.

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CHAPTER II

RHODIUM(I)-TRICYCLOHEXYLPHOSPHINE COMPLEXES AND THEIR REACTIONS WITH UNSATURATED MOLECULES

IIA. SOME ADDUCTS OF $RhCl[P(C_6H_{11})_3]_2$, A RHODIUM COMPOUND SPONTANEOUSLY COORDINATING DINITROGEN*

H.L.M. VAN GAAL, F.G. MOERS AND J.J. STEGGERDA

SUMMARY

Solutions of $RhCl(PCy_3)_2$ react with O_2, N_2, C_2H_4, CO and H_2 to give *trans*-$RhClA(PCy_3)_2$ (A = O_2, N_2, C_2H_4 and CO, Cy = cyclohexyl) and $RhClH_2(PCy_3)_2$; the spontaneous formation of the rather air-stable $RhCl(PCy_3)_2N_2$ is ascribed to a combination of the steric requirements and electronic properties of the phosphine ligand.

Tricyclohexylphosphine (PCy_3), like other bulky phosphines, is effective in stabilizing unusual coordination numbers and valence states[1,2]. In the reaction of PCy_3 with $RhCl_3 \cdot 3H_2O$ no reduction to the Rh(I) valence state occurs, but instead inter alia $Rh(II)Cl_2(PCy_3)_2$ is formed[2]. Although the existence of $Rh(III)Cl_3(PCy_3)_3$ has been reported[3], we did not succeed in its preparation and we have not found an indication for a PCy_3/Rh ratio exceeding 2 in any other complex. In this paper we report the preparation of Rh(I)tricyclohexylphosphine compounds by cyclooctene displacement from $[RhCl(C_8H_{14})_2]_2$[4].

Addition of two moles of PCy_3 per mole of $[RhCl(C_8H_{14})_2]_2$ resulted in the rapid formation of ochrous

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$[RhCl(PCy_3)(C_8H_{14})]_2$ (1). The solvated C_8H_{14}-free complex $RhCl(PCy_3)_2(S)$ (S = solvent molecule) was rather slowly formed (20 min stirring) by reaction of either 4 moles or an excess (8 moles) of PCy_3 (Rh/PCy_3 = 1/2, resp. 1/4) with $[RhCl(C_8H_{14})_2]_2$ in C_6H_6, and was isolated as a lilac precipitate of yet not fully identified nature. When $[RhCl(C_2H_4)_2]_2$ was used, yellow *trans*-$RhCl(C_2H_4)(PCy_3)_2$ (2) was obtained. The lilac product is unstable in the solid state, it decomposes within a few hours under vacuum and somewhat more slowly under nitrogen. It immediately turns brown upon exposure to air. In solution, however, $RhCl(PCy_3)_2(S)$ reacts rapidly with oxygen to give the grayish-blue adduct *trans*-$RhCl(O_2)(PCy_3)_2$ (3), while the dinitrogen adduct *trans*-$RhCl(N_2)(PCy_3)_2$ (4) is formed when a solution of $RhCl(PCy_3)_2(S)$ is exposed to 1 atm of N_2 for five days. CO equally adds to $RhCl(PCy_3)_2(S)$ to yield the known *trans*-$RhCl(CO)(PCy_3)_2$ (5)[2].

$RhCl(PCy_3)_2(S)$, made in situ, catalyses the hydrogenation of cyclohexene in benzene at a rate which is about 40 times less than the rate of hydrogenation by $RhCl(PPh_3)_3$ under similar conditions[5]. The yellow dihydride $RhClH_2(PCy_3)_2$ (6) and the corresponding $RhClD_2(PCy_3)_2$ (7) can most conveniently be prepared by the reaction of $RhCl(PCy_3)_2(C_2H_4)$ with H_2 or D_2.

Satisfactory analyses of the compounds have been obtained. Infrared spectroscopic data are given in Table 1. The large variation in Rh-Cl stretching vibration frequencies suggests that in the complexes $RhClA(PCy_3)_2$, Cl and A are in *trans* positions as are the two bulky PCy_3 ligands. The dihydride (6) has a different structure and its Rh-Cl stretching vibration frequency may not be compared with those of the other adducts.

We assume the bulkiness of tricyclohexylphosphine to be one of the causes of the formation of the dinitrogen adduct (4). For PCy_3, neither formation of a *tris*-complex comparable to $RhCl(PPh_3)_3$[5] nor of a dimer comparable to [RhCl-

TABLE 1

INFRARED SPECTROSCOPIC DATA FOR COMPOUNDS $RhCl(PCy_3)_2A$

A	IR absorptions (cm^{-1})	
	ν(Rh-Cl)	others
C_2H_4	294m	3077w, 3040w, 3017w (ν(CH)); 1510w (br), 1208m, 1183w; 950m, 933w (δ(CH))
CO	304m	1942vs (ν(CO)), 584s (δ(CO))
N_2	317m	2103vs (ν(NN)), 470m (ν(RhN))
O_2	328m	993m[a]
H_2	291m	2165(sh), 2120m (ν(Rh-H)), 622m(br)(δ(Rh-H))
D_2	291m	1560(sh), 1528m (ν(Rh-D))

[a] Not assigned. PCy_3 absorbs in the 800-900 cm^{-1} region where MO_2 modes normally are found[7].

$(PPh_3)_2]_2$[5] seems possible. Also adducts with C_6H_6 or C_8H_{14}, the other molecules present, seem to be labilized by steric influences of the two PCy_3 ligands. We therefore postulate the transient existence of the 14 metal valence electron species $RhCl(PCy_3)_2$ as the N_2-bonding species to account for this spontaneous dinitrogen coordination, which has not been reported before for rhodium(I) complexes. The comparable rhodium-dinitrogen compound $RhCl(PPh_3)_2(N_2)$ has been prepared by an indirect method[6]. The high basicity of PCy_3 may facilitate the addition of N_2, and certainly improves the stability of $RhCl(PCy_3)_2(N_2)$, which is only partly decomposed by air upon standing overnight in C_6H_6 or $CHCl_3$. At room temperature the N_2-ligand can be replaced by CO, but not by C_2H_4 or H_2. In similar reactions CO displaces C_2H_4, H_2, and O_2 from their adducts, to yield spectroscopically pure (5). Oxygen slowly replaces C_2H_4 and H_2 to give

impure (3). In contrast to the behaviour of $RhCl(PPh_3)_2A$ ($A = C_2H_4$ or H_2)[5], $RhCl(PCy_3)_2A$ appears not to lose its coordinated molecule of C_2H_4 or H_2 on sweeping its solution with nitrogen.

A mixture of $[IrCl(C_8H_{14})_2]_2$[4] and PCy_3 in C_6H_6 does not coordinate dinitrogen. Reactions with this system and further reactions with the rhodium system are currently under investigation.

We thank Mr. J. Diersmann for the elemental analyses and Mr. A.W.P.G. Peters-Rit for the kinetic measurements.

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IIB. FLUORODICYCLOOCTENERHODIUM(I), A VERSATILE RHODIUM COMPLEX*

H.L.M. VAN GAAL, F.L.A. VAN DEN BEKEROM AND J.P.J. VERLAAN

SUMMARY

$[RhF(C_8H_{14})_2]_n$ has been prepared and used in the synthesis of $RhF(PPh_3)_3$ and of other halo-, phosphine-, carbonyl- and/or dinitrogen-containing rhodium(I) complexes.

Rhodium(I)-olefin complexes are used as starting materials[1,2] for the preparation of a great variety of rhodium compounds, both by nucleophilic (Lewis base) displacement[3] and by oxidative displacement of the olefin[4]. Monoolefins are superior to diolefins as the latter cannot always be displaced, *e.g.* by tertiary phosphines[5]. In preparative rhodium chemistry, metathesis of a chloro ligand is interesting, but often difficult to realize, but this metathesis problem has been overcome by the use of the easily displacable fluoro ligand in $RhF(CO)(PPh_3)_2$[6]. This complex, the only previously known fluororhodium compound, was prepared from $RhCl(CO)(PPh_3)_2$ and AgF.

We now report the preparation of a novel fluoro-olefin complex of rhodium(I), $[RhF(C_8H_{14})_2]_n$ (1) (C_8H_{14} = cyclooctene), which is easy to handle, and which, by the presence of good leaving ligands, is particularly useful for synthetic purposes. A few examples of its use are given.

$[RhF(C_8H_{14})_2]_n$ is synthesized under nitrogen by stirring 1.0 g (3 mmol) $[RhCl(C_8H_{14})_2]_2$ (prepared according to ref. 1) and 0.8 g (6.3 mmol) AgF (Fa. Merck) in acetone in the dark for 2½ h. The black precipitate is collected on a

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filter, and extracted with 100 ml benzene. The solution is filtered over Hyflo and concentrated at reduced pressure, and hexane is added. The yellow precipitate is filtered off and dried under vacuum. Yield 60-75%, analysis: Found: C 52.68; H 7.98; Cl 0.52; F 5.41. $C_{16}H_{28}FRh$ calcd.: C 56.14; H 8.24; Cl 0.00; F 5.55%. Apparently the compound is contaminated with a few percent of the AgF·AgCl double salt[7], which does not interfere much in its reactions. (1) can be stored in air for over a month at room temperature, and longer in the cold. It probably has a dimeric fluoro-bridged structure*. The chlorine metathesis of $[RhCl(C_8H_{14})_2]_2$ with $AgNO_3$ and $Ag(CH_3COO)$ led to less complete displacement of Cl, and the formed cyclooctene complexes were less stable than (1).

The reaction of phosphines, CO, N_2 and sodium halides with (1) have been studied. $RhF(PPh_3)_3$ (2) was isolated from the reaction of (1) with PPh_3 in benzene by precipitation with hexane. Analyses: Found: C 70.09; H 5.24; calcd.: C 70.19; H 5.20%. The compound must be stored under nitrogen; in air $OPPh_3$ is slowly formed. As a hydrogenation catalyst (cyclohexene in benzene, 25°C, P_{H_2} 100 cmHg, $[c_0]$ 4 x 10^{-3} mol/l (2) is initially slightly more active than $RhCl(PPh_3)_3$[8], $-dH_2/dt$ = 5.5 x 10^{-4} and 5.2 x 10^{-4} mol/l *sec*, respectively, but its activity falls within 25 minutes to about 15%. (It is noteworthy that an attempted synthesis of (2) from $RhCl(PPh_3)_3$ and AgF failed[9]). Treatment of (2) with CO leads to $RhF(CO)(PPh_3)_2$; similarly, treatment of (1) with PCy_3 (Cy = cyclohexyl) and CO results in $RhF(CO)(PCy_3)_2$. Analysis: Found: C 60.62; H 9.14; calcd.: C 62.52; H 9.36%. ν(Rh-F) 470, ν(CO) 1936 and δ(RhCO) 606 cm^{-1}.

Reaction of (1) in benzene with an aqueous solution of NaBr gives an orange benzene layer presumably containing $[RhBr(C_8H_{14})_2]_n$, which is too unstable to isolate. Freshly

* Such a structure was recently found for $[CoF(C_5H_5N_2)_3]_2(BF_4)_2$[12].

prepared in solution, it has been used to synthesize $RhBr(PPh_3)_2(CO)$. Addition of NaI in water to a benzene solution of (1) leads to immediate decomposition of (it is assumed) $[RhI(C_8H_{14})_2]_n$. If first phosphine and then a sodium halide is added to (1), both olefin displacement and fluorine metathesis can be readily achieved, and in this way $RhBr(PCy_3)_2$ and $RhI(PCy_3)_2$ have been prepared. The best demonstration of the versatility of (1) is the one-step synthesis of $RhX(PCy_3)_2(N_2)$ (X = Br, I) from (1), PCy_3, NaX and molecular nitrogen. Full details of these reactions will be reported later. Dinitrogen coordination by a rhodium(I) complex is known for the reaction of $RhCl(PCy_3)_2$ with N_2[10].

The thermal stability of $[RhF(C_8H_{14})_2]_n$ is consistent with the stability order often found for Group VIIIb and VIIIc halo-olefin complexes[11], *e.g.* Cl>Br>I. If chelating ligands are included, the order of stability of $[RhX(C_8H_{14})_2]_n$ complexes is: $F>Cl>Et_2NCS_2^- >CH_3COO\sim NO_3>Br(>I)$.

It is clear that $[RhF(C_8H_{14})_2]_n$ is a useful starting material for the synthesis of novel fluororhodium(I) complexes, and more generally for rhodium compounds containing a variety of anionic ligands in cases when direct chlorine replacement may fail.

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IIC. THREE-COORDINATE $RhX[P(C_6H_{11})_3]_2$, THEIR REACTIONS WITH N_2 AND O_2, AND THE *TRANS*-INFLUENCE IN $RhX[P(C_6H_{11})_3]_2L$ (X = anionic, L = neutral ligand)*

H.L.M. VAN GAAL AND F.L.A. VAN DEN BEKEROM

SUMMARY

Three-coordinate $RhX(PCy_3)_2$ complexes (X = F, Cl, Br, I; Cy = cyclohexyl) have been prepared from Rh(I) cyclooctene compounds. $RhCl(PCy_3)_2$ is in equilibrium with its dimer. The complexes $RhX(PCy_3)_2$ (X = Cl, Br, I) form the adducts $RhX(PCy_3)_2(N_2)$ with dinitrogen, the reaction times of N_2-fixation being 4 days, 3 hours and 15 minutes respectively. The three-coordinate complexes form four-coordinate dioxygen adducts $RhX(PCy_3)_2(O_2)$ which are remarkable for their high $\nu(O=O)$ at about 990 cm^{-1}. This high frequency is explained by the four-coordination, which is exceptional for dioxygen complexes. From $RhF(PCy_3)_2$ carbonyl, ethene and diphenylacetylene complexes $RhX(PCy_3)_2L$ (X = F, Cl, Br, I, N_3, NCO, NCS: L = CO, C_2H_4, C_2Ph_2; X = CN, NO_3, acetate: L = CO) have been prepared. The order of the infrared frequencies of the neutral ligands is approximately F<Cl<Br<I and N_3<NCO<NCS<CN for the CO, C_2H_4 and N_2 complexes, and I<Cl<Br<F and N_3<NCO<NCS for the C_2Ph_2 and O_2 complexes. These different orders are discussed considering the different π-bonding properties of the X-ligands and of the L-ligands.

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Rhodium(I)-phosphine complexes catalyse a great variety of organic reactions. Often a three-coordinate species of the type $RhCl(PR_3)_2$ has been invoked as an intermediate during catalytic processes[1-4], but proofs for such a three-coordinate complex were lacking[4]. Although three-coordinate rhodium(I)-carborane complexes $Rh(carborane)(PPh_3)_2$ have been claimed[5], a crystal structure showed that such a complex contained a chelating carborane with a rhodium-carbon bond and a Rh-H-B bridge bond[6].

We have studied the chemistry of rhodium complexes with the bulky ligand tricyclohexylphosphine (PCy_3) which can stabilise unusual coordination numbers and valence states of the rhodium[7-11]. In a preliminary note[7] we postulated the existence of the three-coordinate complex $RhCl(PCy_3)_2$, prepared from $[RhCl(C_8H_{14})_2]_2$[12] (C_8H_{14}=cyclooctene) and PCy_3. This complex formed the adduct $RhCl(PCy_3)_2(N_2)$[7] with molecular nitrogen. With molecular oxygen, the complex $RhCl(PCy_3)_2(O_2)$[7] was formed. This complex had an infrared band at 993 cm^{-1}, an unusual frequency for an O_2-ligand vibration[13]. The synthesis of $[RhF(C_8H_{14})_2]_n$[8] made it possible to prepare similar (pseudo)halo-bistricyclohexylphosphine rhodium(I)-complexes and to study their reaction with nitrogen and oxygen, as well as with carbon monoxide, ethylene and diphenylacetylene. A full report of these reactions is given in this paper.

EXPERIMENTAL

Infrared spectra were measured on a Perkin Elmer 283 spectrophotometer (4000-200 cm^{-1}), equipped with a digital frequency counter. Samples are prepared in KBr or CsI pellets, in nujol between CsI plates, or in benzene between NaCl plates. Fourier transformed ^1H and $^{31}P\{^1H\}$NMR spectra

were recorded on a Varian XL 100 spectrometer at 100 and 40.5 MHz respectively. Air-sensitive compounds were sampled for ^{31}P NMR under helium in 12 mm sample tubes which were subsequently vacuum sealed. C, H and N analyses were carried out at the microanalytical department of this university; the analytical results are given in Table 1. Reactions were carried out with analytical grade reagents and under argon unless otherwise stated. $[RhCl(C_8H_{14})_2]_2$ and $[RhF(C_8H_{14})_2]_n$ were prepared as described in ref. 12 and ref. 8, respectively.

$[RhX(PCy_3)(C_8H_{14})]_n$ (X = F, Cl, Br, I):

91 mg (0.31 mmol) PCy_3 is stirred for 30 minutes with 109 mg $[RhF(C_8H_{14})_2]_n$ or 116 mg (0.155 mmol) $[RhCl(C_8H_{14})_2]_2$ in 10 ml acetone. For the bromo- and iodo-complexes, 25 mg LiBr or NaI is added to the fluoro-complex and the mixture is stirred for another 30 minutes. The complexes $[RhX(PCy_3)(C_8H_{14})]_n$ are isolated by filtration, washed with acetone and dried under vacuum.

$RhX(PCy_3)_2$ (X = F, Cl, Br, I):

a) 182 mg PCy_3 and 109 mg $[RhF(C_8H_{14})_2]_n$ or 116 mg $[RhCl(C_8H_{14})_2]_2$ are stirred for 30 minutes in 10 ml benzene. For X=Br or X=Cl, 25 mg LiBr or NaI is added to the fluoro-complex and the mixture is stirred for another 15 minutes, whereupon the inorganic salts are removed by filtration. Acetone (X = F, Cl) or hexane (X = Br, I) is added and the formed precipitate (X = F: red; X = Cl, Br, I: lilac) is collected on a filter, washed with acetone (X = F, Cl) or hexane (X = Br, I).
b) $RhCl(PCy_3)_2$ may also be prepared by stirring the required equivalents of $[RhCl(C_8H_{14})_2]_2$ and PCy_3 in acetone for 30 minutes or in hexane for 4 hours. The reaction of $[RhF(C_8H_{14})_2]_n$ and PCy_3 in acetone or hexane results in $[RhF(PCy_3)(C_8H_{14})]_n$, $RhF(PCy_3)_2$ is not formed. When acetone

is used in the preparation of $RhBr(PCy_3)_2$ or $RhI(PCy_3)_2$, large percentages of $RhX(PCy_3)_2(CO)$ (X = Br, I) are formed, probably due to decarbonylation of CH_3OH, present in the acetone. Solid $RhX(PCy_3)_2$ (X = F, Cl, Br, I) is immediately decomposed on contact with air. The complexes degrade slowly even under an inert atmosphere. In solution, the decomposition products are, among others, $RhX_2(PCy_3)_2$ (X = Cl, Br)[10] and $RhHX_2(PCy_3)_2$ (X = Cl, Br, I)[10].

$RhX(PCy_3)_2(N_2)$ (X = Cl, Br, I):

$RhX(PCy_3)_2$ in benzene (about 150 mg in 10 ml) is stirred at room temperature under 1 atmosphere nitrogen, till the original colour has disappeared. Acetone is added, the precipitate is collected on a filter, washed with acetone and dried under vacuum. $RhCl(PCy_3)_2$, either isolated from acetone and dissolved in benzene, or prepared in situ in benzene, needs 4 to 5 days for the reaction with N_2; $RhBr(PCy_3)_2$ and $RhI(PCy_3)_2$, both prepared in situ, need respectively about 3 hours and just 15 minutes for this reaction; and $RhF(PCy_3)_2$ shows no addition product with N_2 even after one month. A suspension of $RhCl(PCy_3)_2$ in acetone or hexane does not react with N_2, whereas suspensions of $RhBr(PCy_3)_2$ and $RhI(PCy_3)_2$ do react. $RhX(PCy_3)_2(N_2)$ is contaminated with $RhX(PCy_3)_2(CO)$, $RhHX_2(PCy_3)_2$[10] (X = Cl, Br, I) and $RhX_2(PCy_3)_2$[10] (X = Cl, Br). The contaminants may be responsible for the pale green (X = Cl, Br) or orange (X = I) colour of samples of $RhX(PCy_3)_2(N_2)$.

$RhX(PCy_3)_2(O_2)$ (X = Cl, Br, I, N_3), $RhCl(PCy_3)_2(^{18}O_2)$:

A benzene solution of $RhF(PCy_3)_2$ is stirred with NaX (X = Br, I, N_3) for about 30 minutes. The inorganic salts are removed by filtration. The resulting solution, or a solution of $RhCl(PCy_3)_2$ respectively (about 150 mg in 10 ml benzene), is connected with a small volume of O_2, and gent-

T A B L E 1

ANALYTICAL DATA

(calculated values in parentheses)

Compound	%C	%H	% others
$[RhF(C_8H_{14})(PCy_3)]_2$	59.5 (60.9)	9.45 (9.24)	
$[RhCl(C_8H_{14})(PCy_3)]_2$	59.2 (59.9)	9.42 (8.96)	
$RhCl(PCy_3)_2$	59.7 (61.8)	9.29 (9.52)	P: 7.71 (8.86) Cl: 4.39 (5.07)
$RhBr(PCy_3)_2$	55.0 (58.1)	8.60 (8.95)	P: 8.96 (8.33) Br: 11.98 (10.74)
$RhI(PCy_3)_2$	53.4 (54.7)	8.43 (8.41)	P: 7.05 (8.33) I: 14.47 (16.04)
$RhCl(PCy_3)_2(N_2)$	59.5 (59.5)	9.31 (9.14)	N: 3.06 (3.85)
$RhBr(PCy_3)_2(N_2)$	56.6 (56.0)	8.93 (8.62)	N: 2.68 (3.62)
$RhI(PCy_3)_2(N_2)$	53.4 (52.8)	8.30 (8.13)	N: 2.96 (3.42)
$RhCl(PCy_3)_2(O_2)$	59.9 (59.1)	9.16 (9.10)	
$RhBr(PCy_3)_2(O_2)$	58.9 (55.7)	9.06 (8.58)	
$RhI(PCy_3)_2(O_2)$	49.2 (5.26)	7.57 (8.09)	
$RhF(PCy_3)_2(CO)$	60.6 (62.5)	9.14 (9.36)	
$RhI(PCy_3)_2(CO)$	56.0 (54.3)	8.47 (8.13)	
$Rh(N_3)(PCy_3)_2(CO)$	59.1 (60.6)	8.67 (9.07)	N: 5.25 (5.72)
$Rh(NCS)(PCy_3)_2(CO)$	61.8 (60.9)	9.29 (8.87)	N: 1.63 (1.87)
$Rh(NO_3)(PCy_3)_2(CO)$	56.8 (58.9)	8.47 (8.83)	N: 1.90 (1.86)

to be continued

continued

Compound	%C	%H	% others
$Rh(CH_3COO)(PCy_3)_2(CO)$	61.5 (62.4)	9.30 (9.26)	
$RhF(PCy_3)_2(C_2H_4)$	62.8 (64.2)	9.68 (9.93)	
$RhCl(PCy_3)_2(C_2H_4)$	63.0 (62.8)	9.62 (9.70)	
$RhBr(PCy_3)_2(C_2H_4)$	58.7 (59.1)	9.38 (9.14)	
$RhI(PCy_3)_2(C_2H_4)$	57.2 (55.8)	9.21 (8.62)	
$Rh(N_3)(PCy_3)_2(C_2H_4)$	60.8 (62.2)	9.14 (9.61)	N: 5.26 (5.72)
$Rh(NCO)(PCy_3)_2(C_2H_4)$	60.3 (63.8)	9.31 (9.62)	N: 1.55 (1.91)
$RhF(PCy_3)_2(C_2Ph_2)$	68.0 (69.7)	8.87 (9.00)	
$RhCl(PCy_3)_2(C_2Ph_2)$	67.7 (68.5)	8.20 (8.80)	
$RhBr(PCy_3)_2(C_2Ph_2)$	65.8 (65.1)	8.47 (8.41)	
$RhI(PCy_3)_2(C_2Ph_2)$	62.3 (61.9)	8.19 (8.00)	
$Rh(NCS)(PCy_3)_2(C_2Ph_2)$	66.1 (68.1)	8.62 (8.51)	N: 1.59 (1.56)

ly stirred for a few minutes. Acetone is added and the precipitate is collected on a filter, washed with acetone and dried under vacuum. $^{18}O_2$ was allowed to react with about 15 mg $RhCl(PCy_3)_2$ in 2 ml benzene, and $RhCl(PCy_3)_2(^{18}O_2)$ was isolated by vacuum evaporation of the solvent. $RhF(PCy_3)_2$ reacted quickly with O_2 giving $OPCy_3$. $RhX(PCy_3)_2(O_2)$ is blue-green (X = Cl, Br, N_3) or dark red (X = I).

General procedures for the preparation of $RhX(PCy_3)_2L$ (L = CO, C_2H_4, C_2Ph_2; X = various anionic ligands)

a) A benzene solution of $RhF(PCy_3)_2$ is stirred with NaX for several hours. The inorganic salts are removed by filtration. To the resulting solution (or to a solution of $RhF(PCy_3)_2$ or $RhCl(PCy_3)_2$) is added CO, C_2H_4 or tolane. Ethanol is added (L = CO) or the solution is concentrated to a small volume and acetone is added (L = C_2H_4, tolane). The precipitate is collected on a filter, washed with ethanol (L = CO) or acetone (L = C_2H_4, tolane) and dried under vacuum.

b) $RhF(PCy_3)_2L$ (L = CO, C_2H_4 or tolane) is stirred with NaX in benzene for several hours. The inorganic salts are removed by filtration, and the products are isolated as in a).

c) $RhF(PCy_3)_2L$ (L = CO, C_2H_4, tolane) is stirred with NaX in acetone for several hours. The precipitate is collected on a filter, washed with water and acetone, and dried under vacuum.

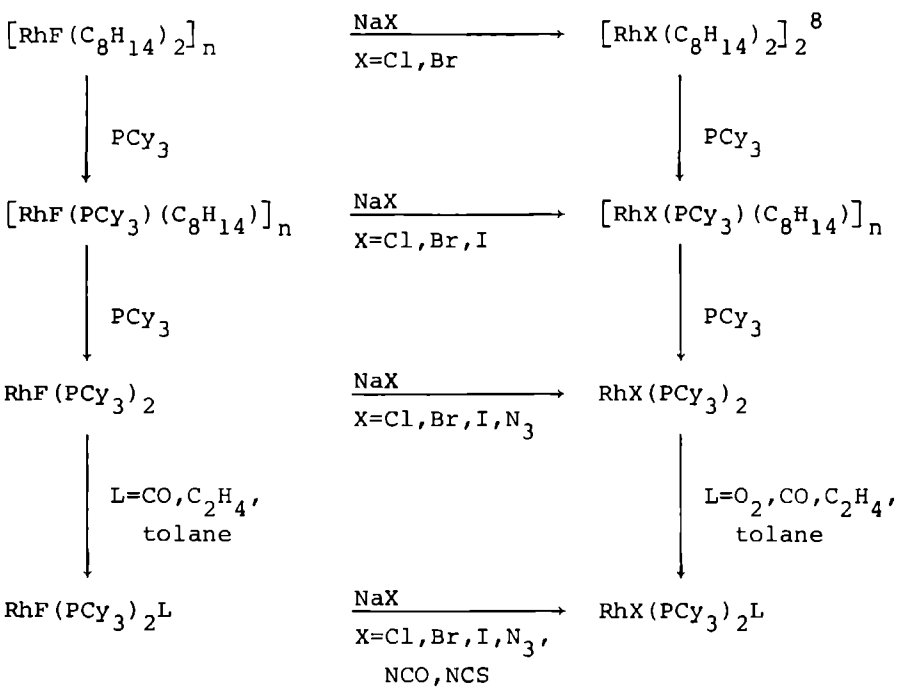
RESULTS AND DISCUSSION

Fluoro-rhodium(I)-complexes

Fluoro-complexes of platinum group metals in low valence states are relatively rare. This has been rationalised in terms of a thermodynamically unfavourable "hard base"-"soft acid" combination[14]. Recently a series of Pd(II) and Pt(II) fluoro-complexes has been reported[14]. $IrF(PPh_3)_2(CO)$ has been known for some time[15,16] and addition complexes of this compound with π-acidic ligands have been described[16,17]. The only fluoro-rhodium(I) complex till recently was $RhF(PPh_3)_2(CO)$[15]. In a preliminary paper, we reported the preparation and synthetic usefulness of $[RhF(C_8H_{14})_2]_n$[8]. By cy-

T A B L E 2

SURVEY OF REACTIONS



clooctene displacement a variety of fluoro-rhodium complexes may be made, and in this way we prepared the fluoro-analogue of Wilkinson's catalyst, $RhF(PPh_3)_3$[8].

Just as from $[RhCl(C_8H_{14})_2]_2$[7], PCy_3 displaces cyclooctene from $[RhF(C_8H_{14})_2]_n$, forming in a first step $[RhF(PCy_3)(C_8H_{14})]_n$ and in a second step $RhF(PCy_3)_2$. The ^{31}P NMR spectrum and the three-coordination of the latter compound is discussed below. In contrast with $RhCl(PCy_3)_2$, the fluoro-complex does not react with molecular nitrogen. With oxygen $RhF(PCy_3)_2$ forms $OPCy_3$ in solution as well as in the solid state.

Addition complexes of $RhF(PCy_3)_2$ with CO, C_2H_4 and C_2Ph_2 have been prepared. They show ν(Rh-F) at 470, 421 and 462 cm^{-1} (Table 5). $RhF(PCy_3)_2(CO)$ has in the ^{31}P NMR spectrum $^1J(Rh-P)$ = 131 Hz and $^2J(F-P)$ = 20 Hz, comparable with the values of $RhF(PPh_3)_2(CO)$ (Table 3).

All fluoro-complexes have a labile fluoro-ligand, which is displaceable by several other coordinating anions. The fluorine-metathesis is fast in a benzene-water two layer system, but the working up procedures of the products are easier, when the metathesis is carried out in benzene with a suspension of a sodium salt, or in acetone. A survey of reactions is given in Table 2.

Three-coordinate complexes

The compounds $RhX(PCy_3)_2$ (X = F, Cl, Br, I) decompose slowly under an inert atmosphere. Their structure has been derived from ^{31}P NMR data. $RhF(PCy_3)_2$ shows a pair of doublets, with $^1J(Rh-P)$ = 206 Hz and $^2J(F-P)$ = 165 Hz (Table 3). In addition, resonances due to $OPCy_3$ and to excess added PCy_3 are present. The pair-of-doublets pattern excludes a dimer or oligomer with fluorine-bridges. A fourth coordination place may be occupied, however, by a solvent molecule (benzene) or a C-H bond interaction of a cyclohexyl group with the metal. In Table 4 are given the ranges of known values of rhodium-phosphorus and fluorine-phosphorus coupling constants for rhodium complexes and for d^8-fluoro-complexes with triaryl- or trialkylphosphines as function of the coordination number and relative ligand position. In $RhF(PCy_3)_2$, the ^2J-(F-P) value of 165 Hz is much too large to have the two PCy_3 ligands in a 90° *cis* position to the fluorine, and two equivalent PCy_3 ligands cannot occupy the single *trans* position to the fluor-

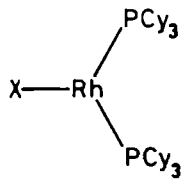


Fig. 1: X - F, Cl, Br, I

TABLE 3

^{31}P NMR DATA OF SOME RHODIUM PHOSPHINE COMPLEXES

Solvent C_6D_6, internal reference PCy_3, δ calculated with respect to trimethylphosphate ($\delta PCy_3 = -7.1$)

Compound	δ, ppm	$^1J(Rh-P)$, Hz	$^2J(F-P)$, Hz
PCy_3	- 7.1		
$OPCy_3$	-44.3		
$RhF(PCy_3)_2$	-55.0	206.0	165.0
$RhI(PCy_3)_2$	-46.1	207.0	
$RhBr(PCy_3)_2$	-45.8	210.0	
$RhCl(PCy_3)_2$	-45.9	209.9	
$RhCl(PCy_3)_2(C_8H_{14})$	-11.2	104.0	
$[RhCl(PCy_3)_2]_2$	-44.4	193.8	
$[RhCl(P(p\text{-Tol})_3)_2]_2$ [a]		196	
$[RhCl(PCy_3)(C_8H_{14})]_2$	-45.1	182.9	
$RhBr(PCy_3)$(norbornadiene)	-28.4	160.8	
$RhHCl_2(PCy_3)_2$ [b]	-32.0	96.2	
$RhCl(PCy_3)_2(O_2)$	-21.0	106.3	
$RhCl(PCy_3)_2(CO)$	-11.9	119.9	
$RhF(PCy_3)_2(CO)$	-10.6	131.0	20.0
$RhF(PPh_3)_2(CO)$ [c]		136	22.0

a) Ref. 4, b) ref. 11; c) ref. 14.

ine (see Tables 3 and 4). These facts strongly suggest trigonal three-coordination of $RhF(PCy_3)_2$ (Fig. 1), without the presence of a solvent molecule or any other coordinating group as a fourth ligand. The three-coordination is further supported by the large $^1J(Rh-P)$ value of 206 Hz, larger than any previously found value for rhodium(I) triaryl- or trialkylphosphine complexes. The value of the ^1J

TABLE 4

^{31}P NMR DATA AND COORDINATION NUMBER

Range of ^{31}P NMR coupling constants of rhodium complexes and of d^8-fluoro-complexes with alkyl- or arylphosphines as function of coordination number and relative ligand position. Data from this work and from ref. 4, 11, 14, 18-20

	$^1J(Rh-P)$			$^2J(F-P)$
	6-coord.	5-coord.	4-coord.	
PR_3 *trans* to PR_3	80-100	95-110	104-153	
PR_3 *trans* to L, $L \neq PR_3$	103-130	145	160-196	
F *trans* to PR_3				139-160
F *cis* to PR_3				20-39

coupling constant is directly related to the s-character of the metal hybrid used in the bonding with the phosphorus. This s-character is determined both by the coordination number and by the relative positions of the ligands. From Table 4, one can see that a value of 206 Hz is reasonable for a three-coordinate species, if one takes into account that in a trigonal geometry the valence angles at the rhodium are neither 90° nor 180°, but somewhere in between.

The major resonances of $RhBr(PCy_3)_2$ and $RhI(PCy_3)_2$ are a doublet with $^1J(Rh-P)$ of 210 and 207 Hz respectively, in addition to minor resonances, attributed to free PCy_3 (added in excess), $OPCy_3$ and $RhHX_2(PCy_3)_2$ (X = Br, I). The ^1J values of $RhBr(PCy_3)_2$ and $RhI(PCy_3)_2$ compare well with the one of $RhF(PCy_3)_2$, which means that the bromo- and the iodo-complex are probably also three-coordinate. The spectra of $RhCl(PCy_3)_2$ are dependent on the conditions of sampling. In addition to the main resonances, resonances from added free PCy_3, $OPCy_3$, $RhHCl_2(PCy_3)_2$, and sometimes RhCl-

$(PCy_3)_2(O_2)$ are present. In concentrated solution the main resonances are a slightly broadened doublet with $^1J(Rh\text{-}P)$ = 193.8 Hz. In diluted solutions an additional doublet with $^1J(Rh\text{-}P)$ = 209.9 Hz is present, and both doublets are broadened. A solution of $[RhCl(C_8H_{14})_2]_2$ and PCy_3 shows a doublet with $^1J(Rh\text{-}P)$ = 104.0 Hz, and a more concentrated solution in addition to this the doublet with ^1J = 193.8 Hz. In the presence of cyclooctene the main resonances are the doublet with the coupling constant of 104 Hz; we therefore ascribe this to $RhCl(PCy_3)_2(C_8H_{14})$. The doublet with coupling constant 209.9 Hz may be ascribed to the monomeric three-coordinate $RhCl(PCy_3)_2$, similar to $RhX(PCy_3)_2$ (X = F, Br, I), and the doublet with J = 193.8 Hz to the dimeric $[RhCl(PCy_3)_2]_2$, in view of its concentration dependance and by comparison with the $^1J(Rh\text{-}P)$ of $[RhCl(P(p\text{-}Tol)_3)_2]_2$ of 196 Hz[4]. The observations can be explained by assuming the following equilibria:

$$\underset{(193.8\ Hz)}{\tfrac{1}{2}[RhCl(PCy_3)_2]_2} \rightleftharpoons \underset{(209.9\ Hz)}{RhCl(PCy_3)_2} \rightleftharpoons \underset{(104.0\ Hz)}{RhCl(PCy_3)_2(C_8H_{14})}$$

In the presence of cyclooctene, the equilibrium lies to the right; in concentrated solutions the equilibrium shifts to the left. In fact, "$RhCl(PCy_3)_2$" is the least soluble from the series $RhX(PCy_3)_2$ (X = F, Cl, Br, I), and concentrated solutions for X = Cl can only be obtained by evaporating cyclooctene from a solution prepared in situ. In this way supersaturated solutions are obtained, from which after a short time $[RhCl(PCy_3)_2]_n$ precipitates. In the far infrared the precipitate shows only a broad Rh-Cl band at 275 cm^{-1}, which does not permit definitive conclusions about its formulation as a dimer in the solid state. The presence of two PCy_3 ligands in a *cis*-configuration is unfavourable on steric grounds, but has its precedent in pseudo square planar $[Pt(allyl)(PCy_3)_2]^+$[21].

Three-coordination is very rare for d^8-metal chemistry. The sp^2-hybridisation in trigonal geometry is unfa-

vourable for d^8, because an empty d-orbital lies near the region of filled d-orbitals (in ideal trigonal geometry the d^8-complex should be paramagnetic with two unpaired electrons). In addition, trigonal geometry leads to relatively weak σ-bonding[22]. It is therefore expected that in the free energy of formation of a four-coordinate adduct the enthalpy contribution generally far exceeds the opposing entropy contribution. However, steric hindrance turns out to be effective in stabilizing this d^8-three-coordination.

That $RhCl(PCy_3)_2$ is in equilibrium with its dimer and with its cyclooctene adduct, indicates that only small free energy differences are involved in the underlying systems. For the bromo- and iodo-complexes, the apparent absence of the analogous equilibria may be caused by the larger covalent radius of the anionic ligand, increasing steric hindrance; in the fluoro-complex it may be caused by a weaker metal-fluoro bond and a more positive metal center.

Dinitrogen coordination

Of the three-coordinate complexes $RhX(PCy_3)_2$, the chloro-, the bromo- and the iodo-complex add molecular nitrogen at room temperature and 1 atmosphere nitrogen. The reaction times of nitrogen-addition are:

$$RhF(PCy_3)_2 + N_2 \quad \text{no reaction}$$

$$RhCl(PCy_3)_2 + N_2 \xrightarrow{\text{4 to 5 days}} RhCl(PCy_3)_2(N_2)$$

$$RhBr(PCy_3)_2 + N_2 \xrightarrow{\text{3 hours}} RhBr(PCy_3)_2(N_2)$$

$$RhI(PCy_3)_2 + N_2 \xrightarrow{\text{15 minutes}} RhI(PCy_3)_2(N_2)$$

The differences in rate of addition may be caused by a higher electron density on the rhodium in the order F<Cl<Br<I, facilitating the nucleophilic attack on the nitrogen[32]. In addition, the rate of the chloro-complex may be influenced by the monomer-dimer equilibrium. Whether the P-Rh-P angle differs among the four complexes and whether

this influences the rates is not known.

The complexes show $\nu(N\equiv N)$ near 2100 cm^{-1}, and $\nu(Rh-N)$ near 460 cm^{-1} (Table 5). The most probable structure is square planar with *trans*-phosphines (Fig. 2). The complexes can be stored over long periods at room temperature under nitrogen. Carbon monoxide displaces N_2 from the complexes; O_2 displaces N_2 slowly from the chloro-complex, but more rapidly from the iodo-complex. Ethylene displaces N_2 from the iodo-complex, but not from the chloro-complex.

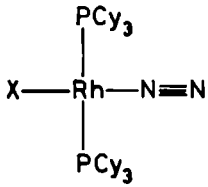


Fig. 2: X = Cl, Br, I

$RhCl(PCy_3)_2$ was the first rhodium compound reported to react spontaneously with nitrogen[7]. The only other case is an unidentified complex with phenyl-5(5H)dibenzophosphole (DBP)[23]. The resulting dinitrogen-containing complex has been formulated tentatively, but probably incorrectly as a six-coordinate rhodium(I)-complex $Rh(BH_3CN)(N_2)(CO)(DBP)_3$.

T A B L E 5

INFRARED DATA OF DINITROGEN AND DIOXYGEN COMPLEXES, cm^{-1}

Compound	$\nu(N_2)/\nu(O_2)$	ν(Rh-N)	others
$RhCl(PCy_3)(N_2)$	2100vs	470s	317(νRh-Cl)
$RhBr(PCy_3)_2(N_2)$	2103vs	462m	
$RhI(PCy_3)_2(N_2)$	2108vs	440s	
$RhCl(PCy_3)_2(O_2)$	993m		328m(νRh-Cl)
$RhBr(PCy_3)_2(O_2)$	991m		
$RhI(PCy_3)_2(O_2)$	986m		
$Rh(N_3)(PCy_3)_2(O_2)$	989m		2053s(N_3)
$RhCl(PCy_3)_2(^{18}O_2)$	943w		328m(νRh-Cl)

The only other rhodium-dinitrogen complex $RhCl(PPh_3)_2(N_2)$[24] has been indirectly prepared from the reaction

$$RhL_n(CO) + RC(O)N_3 \rightarrow RhL_n(N_2) + RC(O)NCO$$

With the same reaction a series of iridium(I)-dinitrogen complexes has been synthesized[25].

Four-coordinate dioxygen complexes

In solution the reaction of $RhX(PCy_3)_2$ with O_2 results in the formation of rather stable dioxygen adducts $RhX(PCy_3)_2(O_2)$, with the exception of $RhF(PCy_3)_2$, which forms $OPCy_3$.

$RhCl(PCy_3)_2(O_2)$ has in its ^{31}P NMR spectrum a $^1J(Rh-P)$ coupling constant of 106.3 Hz (Table 3), in the range of four-coordinate $RhCl(PCy_3)_2L$ complexes, where L is a side-on coordinating ligand[11]. $RhCl(PCy_3)_2(O_2)$ has a single $\nu(Rh-Cl)$ at 328 cm^{-1}, which is a further support of a monomeric four-coordinate structure with side-on coordinated dioxygen (Fig. 3). The complex shows $\nu(^{16}O_2)$ at 993 cm^{-1} and $\nu(^{18}O_2)$ in an $^{18}O_2$ enriched sample at 943 cm^{-1}. The other dioxygen complexes $RhX(PCy_3)_2(O_2)$ (X = Br, I, N_3) have $\nu(O_2)$ at about 990 cm^{-1}. This is an unusual position for the stretching vibration frequency of coordinated O_2. Several reviews have appeared concerning dioxygen complexes[26-29] and, based on infrared data and structures, a division into superoxo complexes ($\nu(O_2)$ ranging from 1075 to 1195 cm^{-1}) and peroxo complexes ($\nu(O_2)$ ranging from 790 to 932 cm^{-1})[26] has been given. The range of h^2-dioxygen complexes runs from 800 to 932 cm^{-1}[26] and the range of h^2-dioxygen-rhodium complexes from 833 to 890 cm^{-1} (data from ref. 29). The $RhX(PCy_3)_2(O_2)$ complexes have $\nu(O_2)$ significantly out of these

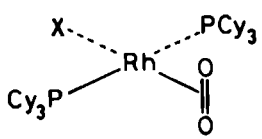


Fig. 3. X = Cl, Br, I, N_3

ranges. The value of 990 cm^{-1} can, however, be explained on the basis of the four-coordination of the complexes.

The d^{10}- and d^8-metal complexes with side-on dioxygen, reported in the literature, which have a well-defined structure, are trigonal or trigonal bipyramidal[28,29]; the $RhX(PCy_3)_2(O_2)$ apparently are the first d^8-square planar dioxygen complexes. For d^6-, d^8- and d^{10}-metal alkyne and alkene complexes a division into class S (square planar and octahedral) and class T (trigonal and trigonal bipyramidal) complexes has been given[30], corresponding to relatively weak and relatively strong π-backbonding. This division is supported by infrared data on alkyne complexes[31] and on tetrafluoroethylene complexes[32] where the stretching vibration frequencies of the coordinated multiple bond in four-coordinate complexes lies significantly above the range of frequencies of five-coordinate complexes. So weak π-backbonding in the four-coordinate complexes $RhX(PCy_3)_2(O_2)$ may explain the O_2 stretching vibration frequency of 990 cm^{-1}, which is unusually high compared with the dioxygen complexes of trigonal or trigonal bipyramidal geometry.

Trans-influence in $RhX(PCy_3)_2L$ (X = anionic, L = neutral ligand

The N_2 and O_2 ligand stretching vibration frequencies have an inverse order in the complexes $RhX(PCy_3)_2L$ (L = N_2, O_2) for X = Cl, Br, I (Table 5). It has been said that "*trans*-influence series derived from vibrational frequencies never agree in detail"[33], but an inverse order for dinitrogen and dioxygen was so much unexpected, that we have explored in some detail the *trans*-influence of a series of anionic ligands on the infrared properties of carbon monoxide, ethene and diphenylacetylene (tolane) in addition to those of dinitrogen and dioxygen.

The complexes are prepared from $RhF(PCy_3)_2$. The expected structures of the complexes are given in Figs. 4-6,

TABLE 6

INFRARED DATA OF CARBONYL, ETHYLENE AND TOLANE COMPLEXES, cm^{-1}

Compound	ν(CO)	δ(CO)	others
$RhF(PCy_3)_2(CO)$	1936s	602s	470m (νRh-F)
$RhCl(PCy_3)_2(CO)$	1947s	582s	305m (νRh-Cl)
$RhBr(PCy_3)_2(CO)$	1947s	574s	
$RhI(PCy_3)_2(CO)$	1948s	564s	
$Rh(N_3)(PCy_3)_2(CO)$	1950s	591s	2067s (N_3)
$Rh(NCO)(PCy_3)_2(CO)$	1950s	592s	2218s (NCO)
$Rh(NCS)(PCy_3)_2(CO)$	1961s	596s	2096s, 836m (SCN)
$Rh(CN)(PCy_3)_2(CO)$	1964s	585s	1945s (CN)
$Rh(NO_3)(PCy_3)_2(CO)$	1953s	593s	1472m, 1288s (NO_3)
$Rh(CH_3COO)(PCy_3)_2(CO)$	1943s	595s	1622s, 1367s (ac)

	δ(CH_2), ν(C=C)	ν(CH)	others
$RhF(PCy_3)_2(C_2H_4)$	1500w, 1200m	940m	421m (νRh-F)
$RhCl(PCy_3)_2(C_2H_4)$	1511w, 1208m	942m	294m (νRh-Cl)
$RhBr(PCy_3)_2(C_2H_4)$	1513w, 1215m	947m	
$RhI(PCy_3)_2(C_2H_4)$	1512w, 1209m	936m	
$Rh(N_3)(PCy_3)_2(C_2H_4)$	1510w, 1209m	940m	2064s (N_3)
$Rh(NCO)(PCy_3)_2(C_2H_4)$	1510w, 1209m	941m	2215s (NCO)
$Rh(NCS)(PCy_3)_2(C_2H_4)$	1514w, 1213m	948m	2085s, 826m (NCS)

	ν(C≡C)	ν_{as}(Rh-C_2)	others
$RhF(PCy_3)_2(C_2Ph_2)$	1868m	585m	462m (νRh-F)
$RhCl(PCy_3)_2(C_2Ph_2)$	1860m	573m	315m (νRh-Cl)
$RhBr(PCy_3)_2(C_2Ph_2)$	1860m	574m	
$RhI(PCy_3)_2(C_2Ph_2)$	1846m	570m	
$Rh(N_3)(PCy_3)_2(C_2Ph_2)$	1856m	570m	2058s (N_3)
$Rh(NCO)(PCy_3)_2(C_2Ph_2)$	1865m	-	2217s (NCO)
$Rh(NCS)(PCy_3)_2(C_2Ph_2)$	1878m	-	2080s, 832m (NCS)

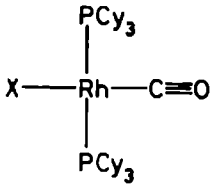


Fig. 4

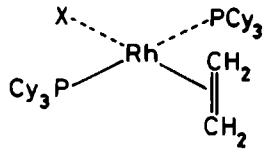


Fig. 5

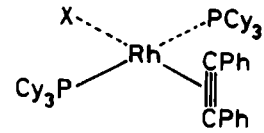


Fig. 6

and infrared spectroscopic data are given in Table 6. Attempts to prepare complexes $RhX(PCy_3)_2(O_2)$ with X = F, NCO, CN or NCS were unsuccessul. Also $Rh(CN)(PCy_3)_2L$ could not be prepared for L = C_2H_4 and C_2Ph_2.

In Table 7 the AB ligand stretching frequencies of the AB molecules (AB = N_2, CO, $H_2C{=}CH_2$, $PhC{\equiv}CPh$, O_2) are given as a measure of the metal-(π-acid) interaction. For the ethene complexes, the sums of the vibrations near 1200 and near 1500 cm^{-1} (the coupled ν(C=C) and δ(C-H) vibrations) are given[34]. The orders of the X *trans* ligands in function of the N_2 and CO frequencies is nearly exactly the same as previously found in other series of square planar $Ir(I)N_2$[35] and Rh(I) and $Ir(I)CO$[35,36] complexes of the type $MX(PR_3)_2L$. There is an increase for the halides from F to I, and a further increase for the pseudo-halides from N_3 and NCO to NCS and CN. The ethene, tolane and O_2 series have no precedent in the Rh(I) and Ir(I) chemistry of four-coordinate complexes. The X-ligand order in the ethene series is comparable with, although not identical with the order in the CO series, and is more or less characterized by an increase for the halides from F to I and for the pseudo-halides from N_3 to NCS. The tolane and O_2 series parallel each other, but do not parallel the CO and ethene series: for the halides there is a tolane and O_2 frequency decrease going from F to I, but for the pseudo-halides there is a frequency increase from N_3 to NCS.

A dominant σ-contribution to the measured *trans*-influence should lead to a similar X-ligand order for the ethene,

TABLE 7

INFLUENCE OF ANIONIC LIGAND X ON THE ν(AB) FREQUENCIES (cm^{-1}) IN $RhX(PCy_3)_2(AB)$ COMPLEXES (AB = N_2, CO, $H_2C{=}CH_2$, $PhC{\equiv}CPh$, O_2)

X \ AB	N_2	CO	C_2H_4*	C_2Ph_2	O_2
F		1936	2700	1868	
Cl	2100	1947	2719	1860	993
Br	2103	1947	2728	1860	991
I	2108	1948	2721	1846	986
N_3		1950	2719	1856	989
NCO		1950	2719	1865	
NCS		1961	2727	1878	
CN		1964			

* For C_2H_4, the sum of the coupled ν(C=C) and δ(C-H) is given[34].

tolane and dioxygen complexes, as these molecules are affected in the same way by σ-bonding. We therefore postulate a dominant π-contribution to the observed *trans*-influence.

The L-ligands differ in their ligand-to-metal π-orbitals: all five possess an empty π-orbital perpendicular to the square plane, the π-orbital in the square plane is empty for N_2 and CO, "non-existing" for ethene, and filled for tolane and O_2. The observed X-ligand orders correspond roughly to (i) the order F<Cl<Br<I and $N_3{\sim}$NCO<NCS<CN for those L-ligands which have only empty π-orbitals (CO, N_2, C_2H_4), and (ii) the order F>Cl>Br>I and N_3<NCO<NCS for those L-ligands which have both empty and filled π-orbitals

(tolane and O_2). The halides are good π-donors by their filled p-orbitals, and have increasing π-acceptor properties in the order (F<)Cl<Br<I by their empty d-orbitals. The pseudo-halides have poor π-donor properties by their filled π-orbitals and rather good π-acceptor properties by their empty π*-orbitals. Apparently, the infrared frequencies of the L-ligands discriminate between these different π-bonding properties of the X-ligands by virtue of their own π-bonding requirements. X-ligands with only π-donor properties (F) or with only π-acceptor properties (the pseudo-halides) do not satisfy either the π-donor or the π-acceptor requirements of the tolane and O_2 ligands. Tolane and O_2 have the best bonding when the *trans*-ligand is a good π-donor in the square plane and a good π-acceptor perpendicular to the square plane at the same time. This nuanced interpretation is suggested to us by the low frequency of the iodo-tolane and iodo-dioxygen complexes. In the carbonyl complexes the π-donor properties of the heavier halides must be shared by their π-acceptor properties. This gives them a position in between the exclusively π-donor fluorine ligand and the π-acceptor pseudo-halides.

Of course, σ-effects are present and may be different for the various X-ligands. Nonetheless, the observed *trans*-influence is readily rationalized by the variations in metal-ligand π-interactions.

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IID. THE COORDINATION OF HETEROCUMULENES AND OTHER UNSATURATED MOLECULES TO $RhCl[P(C_6H_{11})_3]_2$*

H.L.M. VAN GAAL AND J.P.J. VERLAAN

SUMMARY

$RhCl(PCy_3)_2$ (Cy = cyclohexyl) forms four-coordinate addition complexes with CS_2, COS, RNCS (R = methyl, allyl, phenyl and *p*-tolyl) in which the heterocumulene is side-on coordinated by S and C; and with N,N'-di-*para*-tolyl carbodiimide (TolNCNTol) and PhNCO, in which the heterocumulene is side-on coordinated by N and C. EtNCO and CO_2 do not react with $RhCl(PCy_3)_2$. $IrCl(PCy_3)_2(CS_2)$ and $IrCl(PCy_3)_2$(PhNCS) are also described. By sulfur abstraction from the CS_2-complexes $MCl(PCy_3)_2(CS)$ (M = Rh, Ir) is formed. Addition complexes of $RhCl(PCy_3)_2$ with acetylenes RC≡CR (R = phenyl, ethyl, H), SO_2 and nitrosobenzene are also described. $RhCl(PCy_3)_2$(PhNO) contains an end-on coordinated nitrosobenzene. The ^{31}P NMR spectra of the various addition complexes show a Rh-P coupling constant which correlates with the π-acceptor properties of the added molecule.

INTRODUCTION

Heterocumulenes or pseudo-allenes (X=C=Y)(X, Y = S, NR, O) and related compounds) have interesting bonding and reactivity properties as ligands. Often coordination occurs by the lone pair of the hetero-atom, resulting in h^1-coordination[1-3]. Insertion into a M-Z bond (Z = H, R, SR, halide *etc.*) may lead to a pseudo-allyl ligand[1-5]. Remarkable is

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the recent structure report of $[Ir(S_2CPPh_3)(PPh_3)_2(CO)]BF_4$ which revealed that a PPh_3 ligand had migrated to the carbon atom of the CS_2, resulting in the zwitterionic ligand $Ph_3P^+ - CS_2^-$[6]. Dimerisation of CO_2 to a chelating ligand[7] and catalytic trimerisation of isocyanates have been reported[8]. With low-valent metal complexes, h^2 - (side-on) coordination by one of the double bonds may occur. This mode of coordination is fairly easily realised for the C=S fragment of the heterocumulene[1,9], but relatively rare for C=N and C=O fragments. Examples of the latter two include h^2-coordination of azaallene $R_2\overset{+}{C}=\overset{-}{N}=CR_2$ to Mo(0)[10], of ketenimine $RN=C=CR_2$ to Ni(0)[11], Fe(0) and Co(I)[12], of diphenylketene $Ph_2C=C=O$ to Pt(0)[13] and of carbon-dioxide to Ni(0)[14], Mo(0)[15], Rh(I)[16] and Ir(I)[7,16] complexes. Acylisocyanates RC(O)-N=C=O have been found to coordinate either side-on or chelating to Rh(I)[17,18] and Ir(I)[18,19].

The three-coordinate 14-electron complex $RhCl(PCy_3)_2$[20] is a compound with a paradoxical reactivity. On the one hand, compared to $RhCl(PPh_3)_3$ and $[RhCl(PPh_3)_2]_2$[21] it has by the absence of a fourth ligand an enhanced reactivity. This is demonstrated by its spontaneous coordination of molecular nitrogen[20]. On the other hand, the presence of two bulky tricyclohexylphosphine ligands excludes the addition of other bulky ligands to $RhCl(PCy_3)_2$, and restricts the addition of further ligands as soon as a 16-electron configuration has been achieved. This made it attractive to study the addition of heterocumulenes and other unsaturated molecules to $RhCl(PCy_3)_2$ and related compounds, which is the subject of this paper.

EXPERIMENTAL

Infrared spectra were measured on a Perkin-Elmer 257 spectrophotometer (4000 - 625 cm^{-1}) and a Hitachi EPI-L spectrophotometer (700 - 200 cm^{-1}) in KBr or CsI pellets. ^1H and

^{31}P NMR spectra were recorded on a Varian XL 100 spectrometer at 100 and 40.5 MHz. C, H and N analyses were carried out at the microanalytical department of this university; other analyses and molecular weight determinations by Dr. A. Bernhardt, Mikoranalytisches Laboratorium, Elbach über Engelskirchen, Germany. Analytical data are given in Table 1.

Reactions were carried out under nitrogen at room temperature in analytical grade solvents. $[RhCl(C_8H_{14})_2]_2$ and $[IrCl(C_8H_{14})_2]_2$ were prepared as described in ref. 22, $RhCl(PCy_3)_2$ and $RhCl(PCy_3)_2L$ (L = H_2, O_2, C_2H_4, CO and N_2) as in ref. 20.

$RhCl(PCy_3)_2(S=C=X)$, (X = S, NPh, N(p-Tolyl), NAllyl, NMe):

An excess of S=C=X was added to a solution of 200 mg $RhH_2Cl(PCy_3)_2$ in 20 ml benzene. The solution was stirred for a few minutes and concentrated at reduced pressure to a small volume. Ethanol was added, and the precipitate was collected on a filter, washed with ethanol and dried under *vacuum*.

$RhCl(PCy_3)_2(S=C=O)$:

During 30 seconds, SCO was passed through a solution of 200 mg $RhH_2Cl(PCy_3)_2$. The solution was concentrated at reduced pressure, ethanol was added, the precipitate was filtered off, washed with ethanol and dried under *vacuum*.

$IrCl(PCy_3)_2(S=C=X)$, (X = S, NPh):

C_2H_4 was bubbled through a solution of 150 mg $[IrCl(C_8H_{14})_2]_2$ in 20 ml benzene, and 200 mg PCy_3 was added; the solution was stirred for 15 minutes and an excess of S=C=X was added. The solution was stirred for another 5 minutes and concentrated at reduced pressure. Ethanol was added, the precipitate collected on a filter, washed with ethanol and dried under *vacuum*.

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ANALYTICAL DATA AND MOLECULAR WEIGHTS OF COMPLEXES
(theoretical values in parentheses)

compound	colour	%C	%H	%N	%S	Mol. wt.[a]	decomp. temp. °C
$RhCl(PCy_3)_2(CS_2)$	ochrous	57.3	8.65		7.57	810	235
		(57.3)	(8.52)		(8.27)	(774)	
$RhCl(PCy_3)_2(SCNMe)$	ochrous	59.9	9.18	1.61		730	167
		(59.1)	(9.01)	(1.81)		(772)	
$RhCl(PCy_3)_2(SCNPh)$	ochrous	61.1	8.45	1.72	3.63	830	140
		(61.9)	(8.58)	(1.68)	(3.84)	(834)	
$RhCl(PCy_3)_2(SCNTol)$	ochrous	62.6	8.83	1.32			167
		(62.3)	(8.67)	(1.65)			
$RhCl(PCy_3)_2(SCNAllyl)$	ochrous	59.6	9.00	1.87			146
		(60.2)	(8.96)	(1.75)			
$RhCl(PCy_3)_2(SCO)$	ochrous	57.5	8.80				188
		(58.5)	(8.76)				
$IrCl(PCy_3)_2(CS_2)$	ochrous	52.2	8.15		9.28		275
		(51.4)	(7.69)		(7.42)		
$IrCl(PCy_3)_2(SCNPh)$	ochrous	54.7	8.15	1.66		1002	158
		(55.9)	(7.75)	(1.52)		(924)	

$RhCl(PCy_3)_2(CS)$	ochrous	59.8	9.00		5.41	831	249
		(59.8)	(8.95)		(4.31)	(743)	
$RhCl(PCy_3)_2(PhNCO)$	yellow	63.1	8.91	1.73		817	172
		(63.1)	(8.75)	(1.71)		(818)	
$RhCl(PCy_3)_2(TolNCNTol).C_6H_6$	orange	68.2	9.17	2.72		940	164
		(68.4)	(8.67)	(2.80)		(921)	
$RhCl(PCy_3)_2(C_2Ph_2)$	yellow	67.7	8.2				
		(68.5)	(8.8)				
$RhCl(PCy_3)_2(C_2Et_2)$	yellow	63.7	9.6				
		(64.7)	(9.8)				
$RhCl(PCy_3)_2(C_2H_2)$	yellow	63.9	9.47				216
		(62.9)	(9.45)				
$RhCl(PCy_3)_2(SO_2)$	brown	57.2	8.92		4.09	711	192
		(56.7)	(8.72)		(4.20)	(763)	
$RhCl(PCy_3)_2(PhNO)$	yellow	63.5	8.87	1.63			153
		(62.6)	(8.88)	(1.74)			

[a] osmometric in benzene

$MCl(PCy_3)_2(CS)$, (M = Rh, Ir):

200 mg $MCl(PCy_3)_2(CS_2)$ and 80 mg PCy_3 in 20 ml benzene were stirred for 24 hours. Ether was added, which did precipitate $SPCy_3$. The solution was filtered, and hexane was added to the filtrate. The second precipitate was collected on a filter, washed with hexane and dried under *vacuum*.

$RhCl(PCy_3)_2(PhNCO)$:

170 mg $[RhCl(C_8H_{14})_2]_2$ and 250 mg PCy_3 were stirred in 10 ml benzene for 45 minutes. Excess PhNCO was added. The solution was concentrated at reduced pressure, ethanol was added, the precipitate was filtered off, washed with ethanol and dried under *vacuum*. The compound has to be stored in the dark.

$RhCl(PCy_3)_2(TolNCNTol)$, (Tol = para-tolyl):

A freshly prepared portion of $RhCl(PCy_3)_2$ was dissolved in benzene (*ca.* 150 mg in 5 ml). Excess N,N'-di-*para*-tolyl carbodiimide was added and the solution stirred for 5 minutes. Ethanol was added, the precipitate was collected on a filter, washed with ethanol and dried under *vacuum*.

Attempted reaction of $RhCl(PCy_3)_2$ with respectively CO_2, EtNCO:

A freshly prepared portion of $RhCl(PCy_3)_2$ (*ca.* 150 mg) was dissolved in 5 ml benzene. The solution was saturated with CO_2, or an excess of EtNCO respectively was added. The lilac colour of $RhCl(PCy_3)_2$ persisted. When the solution was stirred for some days, $RhCl_2(PCy_3)_2$, the decomposition product of $RhCl(PCy_3)_2$[20], was obtained.

$RhCl(PCy_3)_2(C_2Ph_2)$, $RhCl(PCy_3)_2(C_2Et_2)$ and $RhCl(PCy_3)_2(SO_2)$:

These compounds were prepared similarly to $RhCl(PCy_3)_2$-(PhNCO); SO_2 was passed through the solution for *ca.* 30 sec.

$RhCl(PCy_3)_2(C_2H_2)$ and $RhCl(PCy_3)_2(PhNO)$:

These compounds were prepared similarly to $RhCl(PCy_3)_2$(Tol-NCNTol); C_2H_2 was passed through the solution for not longer than 1 minute, and the working-up time was kept to a minimum. The compounds have to be stored under nitrogen at $-20^{\circ}C$.

RESULTS AND DISCUSSION

Synthetic methods

Most addition complexes $RhCl(PCy_3)_2L$ with L = various ligands can be prepared by simple addition to $RhCl(PCy_3)_2$. Adducts with L = phenyl isocyanate, sulfur dioxide, tolane (= diphenylacetylene) and 3-hexyne may also be prepared using solutions of $[RhCl(C_8H_{14})_2]_2$ and the required equivalents of PCy_3, aged for one hour. In such a solution, the equilibrium $RhCl(PCy_3)_2(C_8H_{14}) \rightleftarrows RhCl(PCy_3)_2 + C_8H_{14}$ lies to the left[20b]. Cyclooctene has to be removed for the reaction of $RhCl(PCy_3)_2$ with N,N'-di-*para*-tolyl carbodiimide, nitrosobenzene and acetylene, whereas even under these conditions ethyl isocyanate and carbon dioxide do not react.

With S=C containing heterocumulenes, the adducts cannot be prepared by the above-mentioned method of direct addition to $RhCl(PCy_3)_2$. These reactions result in destruction of the heterocumulene. The dihydrido complex $RhH_2Cl(PCy_3)_2$, however, reacts smoothly with S=C=X ligands (X = S, O, NR) under formation of the adducts $RhCl(PCy_3)_2(SCX)$ and hydrogen replacement.

The reaction of $[IrCl(C_8H_{14})_2]_2$[22] with PCy_3 leads to the formation of an oily product. $IrCl(C_2H_4)_4$[24] gives with PCy_3 an orange solution, from which impure $IrCl(PCy_3)_2(C_2H_4)$ can be isolated. The solution reacts with carbon disulfide, carbonyl sulfide and phenyl isocyanate, but not with methyl and allyl isocyanate. The iridium-tricyclohexylphosphine system has not been investigated further.

S=C=X heterocumulenes rapidly displace H_2 from $RhH_2Cl(PCy_3)_2$ to form the complexes $RhCl(PCy_3)_2(SCX)$ (X = S, NR or O). $IrCl(PCy_3)_2(SCX)$ (X = S, NPh) has been obtained similarly from $IrCl(PCy_3)_2(C_2H_4)$ and S=C=X. In contrast with $RhCl(PPh_3)_3$[9] two S=C=X molecules never coordinate to $RhCl(PCy_3)_2$.

The complexes are monomeric in benzene. The ^{31}P NMR spectra of the rhodium complexes (Table 4) all show a doublet arising from coupling of two equivalent phosphorus atoms with rhodium (I = ½), which indicate square planar structures with *trans*-phosphines.

All complexes show infrared absorptions (Table 2) characteristic for side-on C=S coordination[1] (Fig. 1): one band between 603 and 649 cm^{-1}, which we attribute to a $\overset{C}{\underset{M}{\diagdown\!\diagup}}\!\!-\!\!S$ ring vibration with ν(M-C) and ν(C-S) character, and another one between 275 and 292 cm^{-1}, which we attribute to a ν(M-S) vibration. ν(M-Cl) is found between 314 and 335 cm^{-1}.

$RhCl(PCy_3)_2(CS_2)$ shows ν(C=S) of the uncoordinated double bond at 1240 and 1186 cm^{-1}, and $IrCl(PCy_3)_2(CS_2)$ at 1264 and 1166 cm^{-1}. Baird *et al.*[9] explained the presence of two bands in this region by the possible occurrence of isomers. We think it more probable that the doubling is caused by Fermi resonance of the overtone of the vibration near 620 cm^{-1}.

$RhCl(PCy_3)_2(SCO)$ has ν(C=O) at 1762 cm^{-1}; the isothiocyanate complexes $RhCl(PCy_3)_2(SCNR)$ (R = methyl, allyl, phenyl and *para*-tolyl) and $IrCl(PCy_3)_2(SCNPh)$ have ν(C=N) between 1659 and 1710 cm^{-1}. ν(CN) increases from phenyl to *p*-tolyl to allyl to methyl.

The CS_2-complexes decompose upon standing in solution by sulfur abstraction. In contrast with $RhCl(PPh_3)_2(CS_2)_2$[25], no polar co-solvent is needed for this sulfur abstraction reaction. When an extra PCy_3 is added to the solution, a high yield of the thiocarbonyl complexes $MCl(PCy_3)_2(CS)$ (M = Rh, Ir) is obtained. $IrCl(PCy_3)_2(CS)$ has been previous-

ly prepared from $IrCl(PPh_3)_2(CS)$ and PCy_3[26]. The thiocarbonyl complexes are supposed to be structurally similar to $RhCl(PPh_3)_2(CS)$[25], the crystal structure of which shows an end-on carbon-coordinated CS-group *trans* to the chlorine ligand (Fig. 2).

From a solution of $RhCl(PCy_3)_2(COS)$, $RhCl(PCy_3)_2(CO)$ is deposited upon standing. Only $IrCl(PCy_3)_2(CO)$ could be isolated from the reaction of $IrCl(PCy_3)_2(C_2H_4)$ and COS. No sulfur-abstraction from the isothiocyanate complexes has been noticed. These latter complexes are also rather resistant towards breaking of the R-N bond, a reaction observed during addition of RNCS towards $Pt(PPh_3)_3$ for various R[9].

RN=C=X heterocumulenes (X = NR, O) and CO_2

$RhCl(PCy_3)_2(PhNCO)$ and $RhCl(PCy_3)_2(TolNCNTol)$ are monomeric in benzene. The ^{31}P NMR spectra show a doublet for both compounds, indicative of two equivalent phosphorus atoms. The $^1J(Rh-P)$ coupling constants of the two complexes are nearly identical (110.5 and 110.6 Hz), which is indicative of a comparable bonding situation (Table 4).

$RhCl(PCy_3)_2(TolNCNTol)$ has CN-stretching vibration bands at 1742 and 1375 cm^{-1}. These values agree with a h^2-coordination *via* C and one N of the carbodiimide, in which the bond order of one C=N bond is lowered upon coordination (see below). This is to our knowledge the first report of a h^2-coordinated carbodiimide (Fig. 3). In $RhCl(CO)_2(carbodiimide)$, the ligand is h^1-coordinated *via* one of the N-atoms[27]. The difference in coordination behaviour must be attributed to the different basicities of the metal centers in the fragments $RhCl(PCy_3)_2$ and $RhCl(CO)_2$.

$RhCl(PCy_3)_2(PhNCO)$ has strong infrared absorption bands at 1333 and 1842 cm^{-1}, atributable to the symmetric and antisymmetric stretching vibrations of the NCO moiety. These values agree with a h^2-coordination of phenyl isocyanate. The coordination is either by carbon and nitrogen or by

T A B L E 2

INFRARED DATA OF COMPLEXES, CM^{-1}

compound	νM-Cl	νM-S	$\nu M\begin{smallmatrix}C\\|\\S\end{smallmatrix}$	νC=N	νC=S	others
$RhCl(PCy_3)_2(CS_2)$	329s	284s	610s		1240s	
					1186s	
$IrCl(PCy_3)_2(CS_2)$	323s	-	625s		1264s	
					1166s	
$RhCl(PCy_3)_2(CS)$	287s				1283vs	
$RhCl(PCy_3)_2(SCNMe)$	329s	277s	610m	1710vs		
$RhCl(PCy_3)_2(SCNAllyl)$	329m	275m	603m	1700s		1640m (νC=C)
$RhCl(PCy_3)_2(SCNPh)$	314m	285w	649s	1680vs		1582s,
						1474s (Ph)
$IrCl(PCy_3)_2(SCNPh)$	314s	-	646m	1659vs		1584s,
						1484s (Ph)
$RhCl(PCy_3)_2(SCNTol)$	335m	292m	644m	1690vs		1604s, 1572w
						1503s (Tol)
					νC=O	
$RhCl(PCy_3)_2(SCO)$	335s	285m	633s		1762s	
$RhCl(PCy_3)_2(PhNCO)$	326s			1333s	1842s	1589s,
						1491s (Ph)

$RhCl(PCy_3)_2(TolNCNTol)$	321s	1375s		1603s, 1502s
		1742vs		1232s (Tol)
			$\nu C\equiv C$	
$RhCl(PCy_3)_2(C_2Ph_2)$	315s		1860m	
$RhCl(PCy_3)_2(C_2Et_2)$	308s		1943m	608m (νRh-C)
$RhCl(PCy_3)_2(C_2H_2)$	302s		1721m	651s (νRh-C)
$RhCl(PCy_3)_2(SO_2)$	292m	1266s, 1121s, 1111s (νS=O), 570vs ($\delta S=O_2$)		
$RhCl(PCy_3)_2)_2(PhNO)$	290w			1357s (νN=O)

Fig. 1: M = Rh, X = S, O, NMe, NAllyl, NPh, N(*p*-Tol); M = Ir, X = S, O.

Fig. 2: M = Rh, Ir.

Fig. 3

carbon and oxygen.

Solid $RhCl(PCy_3)_2(PhNCO)$ must be stored in the dark; under the influence of light it decomposes within a day. As a strong infrared band at 1947 cm^{-1} is observed, the decomposition product may contain $RhCl(PCy_3)_2(CO)$[20]. This implies that a nitrene entity NPh has been split off. The nitrene has, however, not been detected. The decarbonylation of organic isocyanates has recently been reviewed[28]; the example of $RhCl(PCy_3)_2(PhNCO)$ shows that this reaction most probably occurs by a C=N h^2-coordinated intermediate.

Infrared properties of coordinated cumulenes

The stretching vibrations of the two double bonds of allene ($H_2C=C=CH_2$), carbodiimide and phenylisocyanate are coupled in a symmetric vibration near 1200 cm^{-1} and an antisymmetric one near 2000 cm^{-1}. Upon side-on coordination the force constant of the coordinated C=X bond stretching is lowered. In addition, the angle at the central carbon atom is no longer 180°. These two effects alter the coupling between the two stretching vibrations. In Fig. 4 are given the calculated effects of coupling in coordinated allene. It can be seen that the antisymmetric vibration of the allene reflects the lowering of the force constant of the coordinated double bond. This is experimentally confirmed by the results, given in Fig. 5, where the infrared data of a series of allene and diphenylacetylene complexes are compared. In the carbodiimide and phenyl isocyanate complexes both the symmetric (ν_{sym}) and the antisymmetric (ν_{as}) vibrations are found. This permits a rough calculation of the lowering of the frequency of the coordinated double bond (ν_{coord}), corrected for coupling with the uncoordinated double bond ($\nu_{uncoord}$), by the formula:

$$\nu^2_{as} + \nu^2_{sym} = \nu^2_{coord} + \nu^2_{uncoord}$$

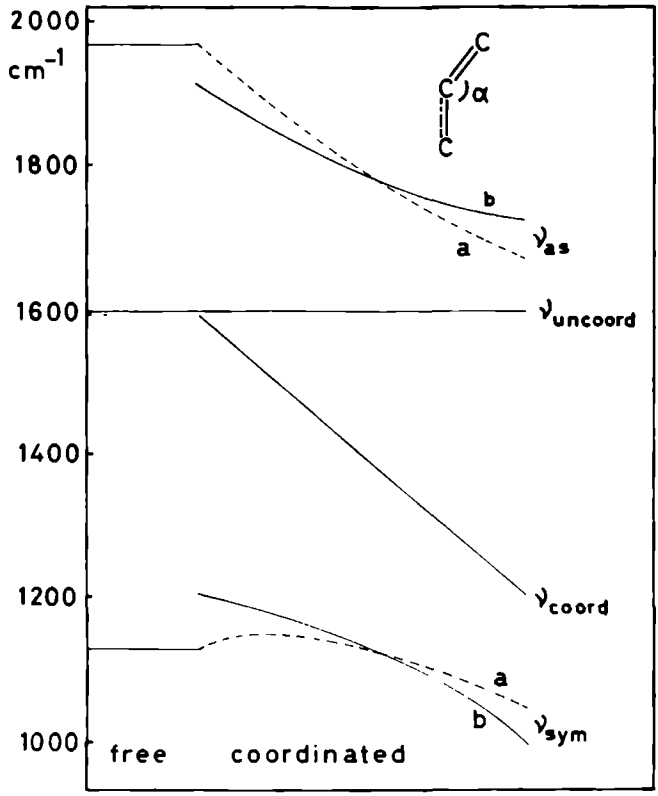


Fig. 4: Calculated coupling between ν_{coord} and $\nu_{uncoord}$ in allene, resulting in ν_{as} and ν_{sym}. ν_{coord} as variable; a: α changing linearly with ν_{coord}; b: α = 150°. The Figure shows that ν_{as} reflects the value of ν_{coord}.

With the estimated values of $\nu_{uncoord}(CN) = 1650\ cm^{-1}$ and $\nu_{uncoord}(CO) = 1720\ cm^{-1}$, an approximate value of ν_{coord} may be calculated. For the carbodiimide, $\nu_{coord}(CN) = 1484\ cm^{-1}$ and the lowering of the CN frequency on coordination is $\Delta\nu\ (CN) = 1650 - 1484\ cm^{-1} = 166\ cm^{-1}$. If, in the phenyl isocyanate complex, CN is coordinated, then $\nu_{coord}(CN) =$

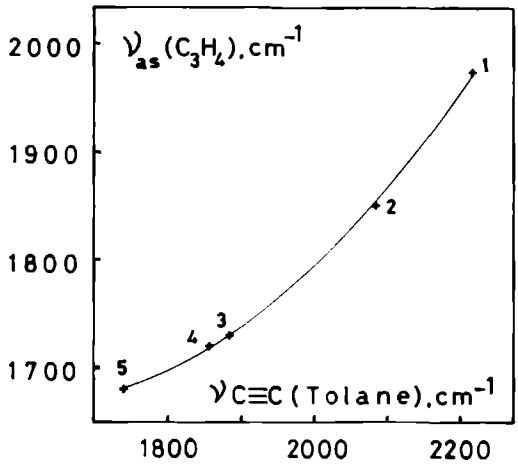


Fig. 5: Comparison of infrared data of allene and tolane complexes. Data from ref. 23, 29-32.

1 free ligand L (L = allene, tolane);
2 $[Pt(CH_3)(PPh_2Me)_2(allene)]^+$ versus $[Pt(CH_3)(AsMe_3)_2(tolane)]^+$;
3 $RhCl(PPh_3)_2L$;
4 $IrCl(PPh_3)_2L$;
5 $Pt(PPh_3)_2L$

1487 cm^{-1} and $\Delta\nu$(CN) = 1650 - 1487 cm^{-1} = 163 cm^{-1}, if CO is coordinated, then ν_{coord}(CO) = 1564 cm^{-1} and $\Delta\nu$(CO) = 1720 - 1564 cm^{-1} = 156 cm^{-1}. These values are a rough measure of the interaction between the metal and the coordinated double bond.

The calculated values of $\Delta\nu$(CN) = 163 cm^{-1} and $\Delta\nu$(CO) = 156 cm^{-1} do not furnish a decisive criterion about whether phenyl isocyanate is CN or CO coordinated. However, two other arguments point to CN coordination (Fig. 6): firstly the ^1J(Rh-P) value is equal for the PhNCO and the TolNCNTol complex; and secondly, neither ethyl isocyanate nor carbon dioxide coordinate to $RhCl(PCy_3)_2$, suggesting that both C=O

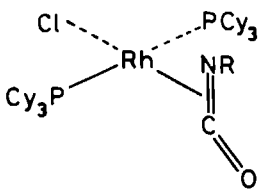


Fig. 6

and C=N h^2-coordination are unfavourable, and that C=N h^2-coordination is promoted by an electron-withdrawing aryl substituent.

Four-coordination

We mentioned that, because of coupling, the antisymmetric vibration frequency of the cumulene ligand measures roughly the interaction between the metal and the coordinated double bond. In sulfur-containing heterocumulenes, the coupling is expected to be weaker, because of the greater mass and/or the larger difference in uncoupled frequencies. Therefore, in sulfur-containing heterocumulenes ν_{as} reflects to a lesser extend the metal-ligand interaction than in allene and in N- and O-containing heterocumulenes. We find, nonetheless, that in the square planar rhodium and iridium PCy_3 complexes the ν_{as} are high, compared with the frequencies of Pt(0) three-coordinate and Rh(I) and Ir(I) five-coordinate complexes of the same ligands (Table 3). This again illustrates that the coordination geometry has a definite influence on the bonding between the metal and a π-acceptor ligand, comparable with the influence of electron density variations, brought about by different ligands. This agrees with the theoretical expectation that trigonal bipyramidal and trigonal complexes have enhanced π-backbonding properties towards ligands in the trigonal plane by symmetry-allowed interplay of the π-acceptor orbitals with the σ-donor orbitals of the other ligands in the plane[33].

That $RhCl(PCy_3)_2$ does not react with CO_2 and EtNCO, but that $IrCl(PMe_3)_3$[7] and $Ni(PCy_3)_2$[14] do coordinate CO_2, may al-

T A B L E 3

COMPARISON OF INFRARED FREQUENCIES OF

3-, 4- AND 5-COORDINATE COMPLEXES OF S=C=X HETEROCUMULENES

Compound (this work)	ν(C=X) (or mean value), cm^{-1}		Compound (ref. 9)
	4-coord	3/5-coord	
$RhCl(PCy_3)_2(CS_2)$	1213	1024	$RhCl(PPh_3)_2(\pi\text{-}CS_2)(\sigma\text{-}CS_2)$
$IrCl(PCy_3)_2(CS_2)$	1215	1157	$IrCl(CO)(PPh_3)_2(CS_2)$
		1151	$Pt(PPh_3)_2(CS_2)$
$RhCl(PCy_3)_2(COS)$	1762	1727	$Pt(PPh_3)_2(COS)$
$RhCl(PCy_3)_2(PhNCS)$	1680	1540	$RhCl(PPh_3)_2(PhNCS)_2$
$IrCl(PCy_3)_2(PhNCS)$	1659	1643	$Pt(PPh_3)_2(PhNCS)$
$RhCl(PCy_3)_2(MeNCS)$	1710	1653	$Pt(PPh_3)_2(MeNCS)$

so be related to the coordination geometry: four-coordination is less favourable for π-backbonding than five- and three-coordination.

Acetylenes, sulfurdioxide and nitrosobenzene

Diphenylacetylene and diethylacetylene add rapidly to $RhCl(PCy_3)_2$. $RhCl(PCy_3)_2(PhC{\equiv}CPh)$ ($\nu(C{\equiv}C)$ = 1860 cm^{-1}) shows as expected for tolane no tendency to react with a second molecule of tolane. $RhCl(PCy_3)_2(EtC{\equiv}CEt)$ ($\nu(C{\equiv}C)$ = 1943 cm^{-1}) is the first isolated 3-hexyne complex of rhodium. That it does not react with a second molecule of 3-hexyne is attributed to the presence of the bulky phosphines. $RhCl(PCy_3)_2$, prepared *in situ*, reacts with acetylene, C_2H_2, but the reaction goes further, leading probably to a metallocyclopentadiene complex $RhCl(PCy_3)_2(C_4H_4)$ ($\nu(C{=}C)$ = 1615 cm^{-1}), which cannot be isolated in pure form, due to a following decomposition reaction. If cyclooctene is first removed from the $RhCl(PCy_3)_2$ solution, the addition of C_2H_2 is faster, which permits isolation of $RhCl(PCy_3)_2(C_2H_2)$ as a yellow compound ($\nu(C{\equiv}C)$ = 1712 cm^{-1}). This compound, like $Pt(PPh_3)_2(C_2H_2)$[34] ($\nu(C{\equiv}C)$ = 1700 cm^{-1}), $Ir(SnCl_3)(PPh_3)_2(CO)(C_2H_2)$[35] ($\nu(C{\equiv}C)$ = 1682 cm^{-1}) and $Os(NO)(CO)(PR_3)_2(C_2H_2)$[36] is among the few group VIII metal complexes of unsubstituted acetylene. The iridium and osmium complexes have an 18-electron configuration which prevents further reaction. The platinum complex has as a three-coordinate complex an optimum for π-backbonding and has therefore not much tendency to coordinate a second acetylene. Furthermore, the bulky phosphine in $RhCl(PCy_3)_2(C_2H_2)$ slows down sufficiently the addition of a second acetylene to permit isolation of the complex.

The single $\nu(Rh-Cl)$ and the doublet in the ^{31}P NMR spectrum are a sufficient proof of a monomeric *trans*-structure of the $RhCl(alkyne)(PCy_3)_2$ complexes. The acetylenes are expected to be situated perpendicular to the coordination plane (Fig. 7).

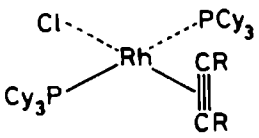
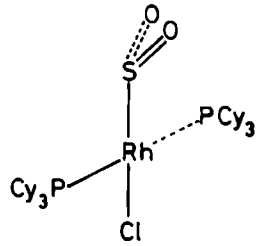


Fig. 7: R = Ph, H, Et.



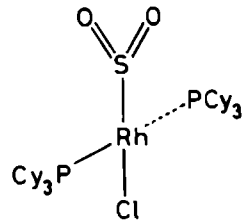


Fig. 8. Possible structures of $RhCl(PCy_3)_2(SO_2)$.

Sulfur dioxide reacts quickly with $RhCl(PCy_3)_2$ to form $RhCl(PCy_3)_2(SO_2)$. This complex does not form a sulfate with oxygen. Conversely, the dioxygen compound $RhCl(PCy_3)_2(O_2)$ does not react with SO_2. According to M.O.-calculations, one expects for a square planar d^8-complex a bent $M-SO_2$-moiety[37], but the infrared frequencies of the SO stretching vibrations at 1266 cm^{-1} (ν_{as}) and 1121, 1111 cm^{-1} (ν_{symm}) agree better with a planar $Rh-SO_2$ group[23] (Fig. 8). We attribute the presence of two absorption bands at the position of the symmetric stretch (near 1120 cm^{-1}) to Fermi resonance doubling, caused by the overtone of the δSO_2 at 570 cm^{-1}.

A clean reaction between PhNO and $RhCl(PCy_3)_2$ could only be obtained if cyclooctene was removed from the reaction mixture. The resulting product $RhCl(PCy_3)_2(PhNO)$ shows $\nu(NO)$ at 1357 cm^{-1}, indicative for N-bonded h^1-coordination[39]. The $^1J(Rh-P)$ value of 153.1 Hz agrees with this h^1-coordination (Fig. 9). PhNO as a ligand is mostly N-bonded[38], but with low-valent metals Fe(0)[39] and Pd(0)[40] side-on coordination to a first metal by N and O with simultaneous bridging to a second metal by N has been found.

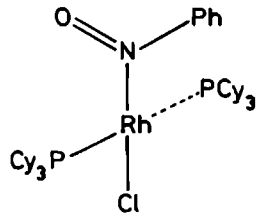


Fig. 9

In Table 4 are collected the ^{31}P NMR data of the four-coordinate addition complexes of $RhCl(PCy_3)_2$. All spectra are characterized by a doublet, caused by coupling with Rh ($I = \frac{1}{2}$), and consequently all complexes possess two equivalent phosphorus nuclei, proving the *trans*-structure for the complexes. We consider the groups of h^2- and of h^1-ligand containing complexes separately.

The chemical shifts show not many regularities, although it may be noticed that for the complexes with h^2-ligands the range of shift-values is smaller (between -14 and -24 ppm) than is the range for the complexes with h^1-ligands (from -9 to -30 ppm).

The $^1J(Rh-P)$ coupling constant contains more information. The group of h^1-ligand containing complexes has on the average a higher coupling constant than the group of h^2-ligand containing complexes. The $^1J(Rh-P)$ value varies regularly with the *cis*-ligand, indicative of a strong *cis*-influence on this value. There is a correlation between π-acceptor strength of the *cis*-ligand and the coupling constant: the coupling constant decreases with increasing π-acceptor strength of the *cis*-ligand, going from PhNO to N_2 to CO to SO_2 for the h^1-ligands, and going from C_2H_4 and acetylenes to RNCX and SCX for the h^2-ligands. Even in fine detail this correlation is present: the coupling constant decreases going from diethylacetylene to acetylene to diphenylacetylene, and going from AllylNCS and MeNCS to TolNCS and PhNCS.

It is likely that changes in coupling constants may be related to changes in the percentage s-character of the rhodium hybride orbital used in the rhodium-phosphorus bond[41]. Various explanations of the observed trends are possible. *(i)* The larger orbital contraction for more positive rhodium centers may have a direct influence on the Rh-P bond and diminish the s(Rh)-character of this bond. *(ii)* The synergic effect, operating both in the rhodium-to-π-acid bond and the

T A B L E 4

^{31}P NMR DATA OF ADDITION COMPLEXES OF $RhCl(PCy_3)_2$

Room temperature, solvent benzene, reference $OP(OMe)_3$

Compound	$^1J(P-Rh)$, Hz	δ, ppm
a) h^2-ligands		
$RhCl(PCy_3)_2(S=CNPh)$	104.4	-18.5
$RhCl(PCy_3)_2(S=CNTol)$	104.6	-17.5
$RhCl(PCy_3)_2(S=CO)$	104.9	-19.1
$RhCl(PCy_3)_2(O=O)$	106.3	-21.0
$RhCl(PCy_3)_2(S=CNMe)$	106.5	-17.8
$RhCl(PCy_3)_2(S=CS)$	106.6	-13.9
$RhCl(PCy_3)_2(S=CN-Allyl)$	106.6	-17.0
$RhCl(PCy_3)_2(PhN=CO)$	110.5	-24.4
$RhCl(PCy_3)_2(TolN=CNTol)$	110.6	-21.6
$RhCl(PCy_3)_2(PhC\equiv CPh)$	115.4	-21.8
$RhCl(PCy_3)_2(HC\equiv CH)$	116.0	-20.3
$RhCl(PCy_3)_2(H_2C=CH_2)$	118.6	-20.0
$RhCl(PCy_3)_2(EtC\equiv CEt)$	121.3	-22.1
b) h^1-ligands		
$RhCl(PCy_3)_2(SO_2)$	107.6	-30.0
$RhCl(PCy_3)_2(CO)$	119.9	-11.9
$RhCl(PCy_3)_2(N_2)$	122.0	-27.6
$RhCl(PCy_3)_2(CS)$	132.1	-16.5
$RhCl(PCy_3)_2(PhNO)$	153.1	- 9.2

rhodium-to-phosphorus bond may be evoked for an explanation of the observed *cis*-influence: the coordination of a strong π-acid may weaken the Rh-P π-bond and by synergism the Rh-P σ-bond; and/or a strong π-bond between rhodium and the *cis*-ligand may strengthen the σ-bond between rhodium and the π-acid, and by competition weaken the Rh-P σ-bond. At least the second part of this argument seems unlikely to us, considering the results we obtained on metal-alkyne complexes, which show that the more strongly π-bonding h^2-ligand tends to be the more weakly σ-bonding h^2-ligand[29]. The first part of argument *(ii)* has been critisized by Venanzi[41], who argued that the metal phosphorus π-bond is too weak to cause by an indirect mechanism such changes in the σ-bond.

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CHAPTER III

OXIDATION OF $RhCl[P(C_6H_{11})_3]_2$ AND AN E.P.R.-STUDY OF SOME RHODIUM(II)-COMPLEXES*

H.L.M. VAN GAAL, J.M.J. VERLAAK AND T. POSNO

SUMMARY

$RhX(PCy_3)_2$ (X = Cl, Br, I; Cy = cyclohexyl) can be oxidized with halogens Cl_2, Br_2 and I_2 to paramagnetic complexes $RhXY(PCy_3)_2$ (X = Cl, Y = Cl, Br, I; X = Y = Br). From $RhX(PCy_3)_2$ and HY the monohydrides $RhHXY(PCy_3)_2$ (X = Cl, Y = Cl, Br, I; X = Y = Br) have been prepared. $RhCl(PCy_3)_2$ reacts with CH_3I to form either $RhMeClI(PCy_3)_2$ or $RhMeI_2(PCy_3)_2$, depending on the reaction conditions. The formation of $RhH_2Cl(PCy_3)_2$ and $RhH_2(BH_4)(PCy_3)_2$ is also described. The stability of the Rh(II) complexes is discussed.

The E.P.R. spectra of $RhXY(PCy_3)_2$ and of $RhCl_2(P(o\text{-}Tol)_3)_2$ (*o*-Tol = *ortho*-tolyl) show large g-anisotropies, with g_{yy} ~4 and g_{xx}, g_{zz} ~1 to 1.6. Two possibilities for the Kramers doublet of the ground state, a mixture of approximately 80% d_z2, 20% d_{xz} and 1% d_{yz}, and a mixture of approximately 80% d_{xz}, 20% d_z2 and 1% d_{xy}, fit the experimental g-values reasonably well.

INTRODUCTION

In a previous paper from this laboratory it was reported that tricyclohexylphosphine (PCy_3) forms paramagnetic complexes $RhX_2(PCy_3)_2$ by reduction of $RhX_3.3H_2O$ (X = Cl,

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Br)[1]. Among the other reported Rh(II) phosphine complexes only $RhCl_2(P(o\text{-}Tol)_3)_2$[2] has a well-defined composition; other compounds, *e.g.* $RhCl_2(P(o\text{-}Tol)_2Ph)_2$[2] and $RhCl_2(P(t\text{-}Bu)_2R)_2$ (R = Me, Et, Pr) (ref. 3, see also ref. 4) seem from their low magnetic moments to be mixtures containing a fraction of paramagnetic complex together with probably a Rh(III)-complex. For the *o*-tolyl complexes E.P.R. g-values strongly deviating from 2 have been reported without interpretation[2]. Interest in the chemistry of paramagnetic Rh(II) with phosphine ligands has arisen from its occurrence during catalytic processes or under circumstances related to catalysis[5-8].

We have extended the investigation of the formation of paramagnetic Rh-PCy_3 complexes to the oxidation of $RhCl(PCy_3)_2$[9] and related complexes. Halogens, hydrogen halides and methyliodide were used as oxidizing agents. Only in the reaction with halogens were Rh(II)-complexes formed. An interpretation of the large g-anisotropy, found in the E.P.R. powder spectra of the Rh(II)-complexes, is given.

During the preparation of this paper, the reaction of $[RhCl(C_8H_{14})_2]_2$ with PCy_3 and HX in CH_2Cl_2 was reported by Betts *et al.*[10], but they did not obtain well-defined products.

EXPERIMENTAL

^1H and ^{31}P NMR spectra were recorded on a Varian XL 100 spectrometer at 100 and 40.5 MHz. E.P.R. spectra were recorded on a Varian E12 E.P.R. spectrometer at X-band; field measurements were done with an A.E.G. Gaussmeter and the frequency was measured with an H.P. 5245 L frequency counter. IR spectra were recorded with a Perkin Elmer 257 (4000 - 700 cm^{-1}) and a Hitachi EPI-L (700 - 200 cm^{-1}) spectrophotometer in KBr and CsI pellets. C, H and N analyses were carried out by Mr. P.J.J. Koonen of this labor-

atory; other analyses were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany. Analytical data are given in Table 1.

All reactions are carried out under nitrogen or argon. $RhCl(PCy_3)_2$[9], $RhBr(PCy_3)_2$[11], $RhI(PCy_3)_2$[11] and $RhCl_2(P(o\text{-}Tol)_3)_2$[2a] were prepared according to the literature.

$RhH_2Cl(PCy_3)_2$ and $RhD_2Cl(PCy_3)_2$:

H_2 or D_2 is bubbled through a solution of $RhCl(PCy_3)_2$ in benzene until the solution becomes yellow. Hexane is added, the precipitate collected on a filter, washed with hexane and dried under vacuum. The compounds are stored under nitrogen at 4°C.

$RhClX(PCy_3)_2$ (X = Cl, Br, I), $RhBr_2(PCy_3)_2$:*

A slight excess of halogen X_2 (0.15 - 0.30 mmol), dissolved in benzene, is added to a solution of 0.30 mmol $RhCl(PCy_3)_2$ in 10 ml benzene. After being stirred for a few minutes, the precipitate is filtered off, washed with benzene and ethanol, and dried under vacuum. $RhBr_2(PCy_3)_2$ is similarly prepared from $RhBr(PCy_3)_2$, but $RhI_2(PCy_3)_2$ could not be obtained from $RhI(PCy_3)_2$ and I_2.

$RhHClX(PCy_3)_2$ (X = Cl, Br, I), $RhHBr_2(PCy_3)_2$, $RhDCl_2(PCy_3)_2$:*

A freshly prepared solution of HX in acetone is added to a suspension of 0.30 mmol $RhCl(PCy_3)_2$ in 10 ml acetone. The precipitate is collected on a filter, washed with acetone and dried under vacuum. The same products are obtained in the reaction of $RhH_2Cl(PCy_3)_2$ with X_2 or HX in benzene or acetone. $RhHBr_2(PCy_3)_2$ is prepared similarly from RhBr-

* The mixed halogen compounds were impure due to scrambling of the halogens.

$(PCy_3)_2$. The deuterated complex $RhDCl_2(PCy_3)_2$ is prepared with DCl in acetone-d^6; it can also be isolated as a side-product to $RhCl_2(PCy_3)_2$ (see ref. 1) from the reaction of $RhCl_3.3H_2O$ and PCy_3 in a D_2O-C_2H_5OD mixture. The compounds are moderately soluble in benzene, and decompose in chlorinated solvents. $RhHCl_2(PCy_3)_2$ has to be stored in the dark; under the influence of light it converts slowly into $RhCl_2(PCy_3)_2$.

$RhHCl_2(py)(PCy_3)_2$.

A few drops of pyridine are added to a suspension of $RhHCl_2$-$(PCy_3)_2$ in benzene. The precipitate is collected on a filter, washed with hexane and dried under vacuum. The compound is insoluble in common solvents.

$RhMeClI(PCy_3)_2$, $Rh(CD_3)ClI(PCy_3)_2$:

A slight excess of CH_3I or CD_3I is added to a suspension of $RhCl(PCy_3)_2$ in hexane. After stirring for 1½ hours, the precipitate is filtered off, washed with hexane and dried under vacuum.

$RhMeI_2(PCy_3)_2$, $Rh(CD_3)I_2(PCy_3)_2$:

A slight excess of CH_3I or CD_3I is added to a benzene solution of $RhCl(PCy_3)_2$. Hexane is added and the precipitate is collected on a filter, washed with hexane and dried under vacuum. The compounds are isolated as benzene solvates.

$RhH_2(BH_4)(PCy_3)_2$:

4.0 mmol $NaBH_4$ is added to a benzene solution of 0.30 mmol $RhCl(PCy_3)_2$. The mixture is stirred for three hours, and ethanol is added. The precipitate is filtered off, washed with ethanol and dried under vacuum.

T A B L E 1

ANALYTICAL RESULTS

Compound	%C	%H	%Cl	others	mol.wt.[a]
$RhH_2Cl(PCy_3)_2$	62.4	9.8			
	(61.7)	(9.8)			
$RhClX(PCy_3)_2$ (X=Cl,Br)	55.2	8.3			
theoretical for X=Br	(55.5)	(8.5)			
$RhClX(PCy_3)_2$ (X=Cl,I)	53.9	8.4			
theoretical for X=I	(52.4)	(8.0)			
$RhHCl_2(PCy_3)_2$	58.7	9.3	9.5	8.3(P)	725
	(58.9)	(8.9)	(9.7)	(8.4)	(733)
$RhDCl_2(PCy_3)_2$	58.6	9.3			
	(58.9)	(8.9)			
$RhHBr_2(PCy_3)_2$	53.5	8.5			
	(52.6)	(8.0)			
$RhHXY(PCy_3)_2$ (X,Y=Cl,Br)	55.5	8.5			
theoretical for XY=ClBr	(55.5)	(8.5)			
$RhHClX(PCy_3)_2$ (X=Cl,I)	54.4	8.6			
theoretical for X=I	(52.4)	(8.0)			
$RhHCl_2(py)(PCy_3)_2$	61.3	8.9		1.6(N)	
	(60.6)	(8.7)		(1.7)	
$RhMeClI(PCy_3)_2$	53.3	8.7	4.1	14.6(I)	851
	(53.8)	(8.3)	(4.2)	(15.1)	(839)
$RhMeI_2(PCy_3)_2 \cdot C_6H_6$	51.7	7.9		24.1(I)	
	(51.1)	(7.5)		(25.0)	
$RhH_2(BH_4(PCy_3)_2$	62.6	10.5			
	(63.5)	(10.7)			

[a] osmometric in benzene

PCy_3 along with $P(o\text{-Tol})_3$ and $P(t\text{-Bu})_3$, is one of the most bulky phosphines used in coordination chemistry[12]. The steric properties of PCy_3 are reflected in the chemical properties of its rhodium complexes.

$RhCl(PCy_3)_2$ is a very air-sensitive compound. It decomposes slowly under an inert atmosphere into $RhCl_2(PCy_3)_2$ and unidentified products. With nitrogen it forms the adduct $RhCl(PCy_3)_2(N_2)$[9]. These observations suggest its formulation as a monomeric three-coordinate Rh(I)-complex, where three-coordination is imposed by the bulkiness of PCy_3 and by the obvious absence of suitable coordinating agents in the mother liquor. $RhBr(PCy_3)_2$ and $RhI(PCy_3)_2$ have similar properties[11].

The addition product of $RhCl(PCy_3)_2$ with hydrogen has a normal stability. The two hydride hydrogens and the two phosphorus atoms are equivalent in the ^1H and ^{31}P NMR respectively (Table 2) and the compound shows two Rh-H stretching vibration frequencies in the IR, one of medium and the other of weak intensity. These data agree with a square pyramidal structure in which the phosphines are *trans* and the chlorine is axially situated (Fig. 1).

Rhodium(II)-complexes

The oxidative addition of halogens to $RhX(PCy_3)_2$ (X = Cl, Br, I) does not yield Rh(III)-complexes, but the paramagnetic $RhXY(PCy_3)_2$ (X = Cl, Y = Cl, Br, I; X = Y = Br). $RhCl_2(PCy_3)_2$ and $RhBr_2(PCy_3)_2$ have previously been prepared by reduction of $RhX_3.3H_2O$ (X = Cl, Br)[1]. This route of oxidation of Rh(I)-complexes has also made possible the preparation of the compounds $RhClBr(PCy_3)_2$ and $RhClI(PCy_3)_2$, which are interesting for E.P.R. study. When different halogens were used, scrambling always was observed. As a con-

T A B L E 2

NMR DATA OF COMPLEXES

Solvent C_6D_6, ambient temperature
Chemical shifts in ppm, coupling constants in Hz
δ relative to trimethylphosphate

^1H NMR[a]

Compound	τ	^1J(Rh-H)	^2J(P-H)
$RhH_2Cl(PCy_3)_2$	32.7	27	14
$RhHCl_2(PCy_3)_2$	not found		
$RhH_2(BH_4)(PCy_3)_2$	26.7 10-17(BH_4)	15[b]	15[b]

^{31}P NMR[c]

Compound	δ	^1J(Rh-H)	^2J(P-H)
$RhH_2Cl(PCy_3)_2$	-47.2	113.7	12
$RhHCl_2(PCy_3)_2$	-32.0	96.2	
$RhH_2(BH_4)(PCy_3)_2$	-52.1	108.3	14

[a] broad signal 7-9 ppm for PCy_3 protons
[b] BH_4-decoupled
[c] partial ^1H-decoupled

sequence, the species with mixed halogens $RhClBr(PCy_3)_2$ and $RhClI(PCy_3)_2$ have been characterised mainly by E.P.R. and IR data. In the reaction of $RhCl(PCy_3)_2$ with Br_2 and I_2 some tendency to form preferentially $RhCl_2(PCy_3)_2$ has been noted.

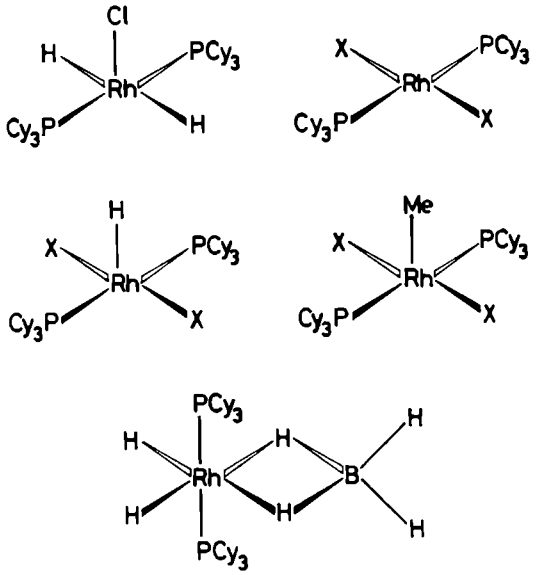

Fig. 1. Proposed structure of complexes. X - Cl, Br or I

We were unable to obtain evidence for the existence of $RhI_2(PCy_3)_2$.

The rhodium(II)-complexes are assigned a square planar *trans*-structure (Fig. 1) on the basis of the high Rh-X stretching vibration frequencies (Table 3). For all complexes, the g-tensor is very anisotropic (Table 4), and the g-values, taken from the E.P.R. powder spectra, are in agreement with such a square planar structure, as is shown below. From the interpretation of these spectra, it was concluded that the E.P.R. spectrum of $RhCl_2(P(o\text{-Tol})_3)_2$ (blue modification)[2] has been incompletely reported and we have remeasured its spectrum, which is also given in Table 4. The magnetic susceptibilities of $RhCl_2(PCy_3)_2$ and $RhBr_2(PCy_3)_2$ have previously been reported[1] and correspond to magnetic moments between 2.2 and 2.3 BM at room tempera-

ture, indicating one unpaired electron, in agreement with the E.P.R. spectra.

It appears that the Rh(II)-complexes have no catalytic activity[4]. $RhCl(PCy_3)_2$, itself a hydrogenation catalyst[9], decomposes slowly into $RhCl_2(PCy_3)_2$. These observations have some significance with respect to the behaviour of catalytic systems containing rhodium and bulky phosphines, *e.g.* polymer phosphines.

Hydrido-Rhodium(III)-complexes

The reaction of $RhCl(PCy_3)_2$ with halogenic acids HX (X = Cl, Br, I) results in the formation of compounds $RhHClX(PCy_3)_2$. Here too, halogen scrambling has been observed. The same products have been obtained from the reaction of $RhH_2Cl(PCy_3)_2$ with HX or X_2. From $RhBr(PCy_3)_2$ and HBr, $RhHBr_2(PCy_3)_2$ has also been prepared.

The mono-hydride complexes show no (Rh-H) stretching vibration band around 2000 cm^{-1}, nor in the PMR spectrum a high field hydride resonance, nor in the partially decoupled ^{31}P NMR spectrum a $^2J(P-H)$ coupling. This is in accord with the properties of $RhHCl_2(P(i\text{-}Pr)_3)_2$[13], where also no Rh-H stretching vibration band nor a hydride NMR resonance could be detected, but it is in contrast with the data reported for $RhHCl_2(P(t\text{-}Bu)_2R)_2$[3], which has ν(Rh-H) at 1938 cm^{-1}, unassigned infrared bands between 570 - 620 cm^{-1} and a hydride NMR resonance at τ = 41.4. The presence of a hydride ligand in our compounds was proven by the reaction with CCl_4, resulting in the formation of chloroform, by the reaction with pyridine, described below, and by a medium-strong infrared absorption at *ca.* 580 cm^{-1}, which we have attributed to a (Rh-H) bending vibration (Table 3). In the deuterated complex $RhDCl_2(PCy_3)_2$ this absorption is absent; the corresponding δ(Rh-D), expected at *ca.* 400 cm^{-1}, is obscured by phosphine-vibrations. However, the second δ(Rh-D) comes

TABLE 3

INFRARED SPECTROSCOPIC DATA, CM^{-1}

Compound	Colour	ν(Rh-X)	ν(Rh-H/D)	δ(Rh-H/D)
$RhH_2Cl(PCy_3)_2$	yellow	291m	2165sh 2120m	622m,br
$RhD_2Cl(PCy_3)_2$	yellow	291m	1560sh 1528m	not found
$RhCl_2(PCy_3)_2$	blue	354s		
$RhClBr(PCy_3)_2$	green	335s 271m		
$RhBr_2(PCy_3)_2$	green	288m		
$RhClI(PCy_3)_2$	brown	325s		
$RhHCl_2(PCy_3)_2$	orange	342s	not found	587s,br
$RhDCl_2(PCy_3)_2$	orange	350s, 335s	not found	350s 335s
$RhHClBr(PCy_3)_2$	orange	330s 280m	not found	580s,br
$RhHBr_2(PCy_3)_2$	orange	268m	not found	580s,br
$RhHClI(PCy_3)_2$	red	320s	not found	579s,br
$RhHCl_2(py)(PCy_3)_2$	ochrous	323s	2135m	not found
			others	
$RhMeClI(PCy_3)_2$	brown	333s	1311w, 1167sh 325m(νRhC)*	
$Rh(CD_3)ClI(PCy_3)_2$	brown	333s	2120m, 2215m(νCD) 755m(νCD), 325m(νRhC)*	
$RhMeI_2(PCy_3)_2$	brown		1167m, 325m(νRhC)*	
$Rh(CD_3)I_2(PCy_3)_2$	brown		2120m, 2215m(νCD) 325m(νRhC)*	
$RhH_2(BH_4)(PCy_3)_2$	white		2102m, 2068m(νRhH) 1926m,br(bridging RhHB) 2450m,br,2400s,br, 2328sh(νBH)	

* tentative assignment

near the ν(Rh-Cl) vibration at 342 cm^{-1} and couples strongly with this vibration, which results in two absorptions at 350 and 335 cm^{-1}. It has been checked with the aid of tabulated G-matrix elements[14] and with the assumption of degenerate ν(Rh-Cl) and ν(Rh-D) vibrations that the observed splitting of 15 cm^{-1} is of the right magnitude. The corresponding ν(Rh-H) is expected at *ca.* 480 cm^{-1}, but is obscured by phosphine absorptions. The δ(Rh-H) value of 580 cm^{-1} is the lowest hitherto reported (*cf.* ref. 15). The unassigned bands between 570 - 620 cm^{-1} reported for $RhHCl_2(P(t\text{-}Bu)_2R)_2$[3] may also be such low-lying δ(Rh-H) vibration frequencies.

The high position of ν(Rh-X) in these compounds and the doublet in the ^{31}P NMR spectrum of $RhHCl_2(PCy_3)_2$ (Table 3) suggest square pyramidal structures with *trans*-phosphines, *trans*-halogens and an axial hydride (Fig. 1). Such a structure has been found in an X-ray analysis of $RhHCl_2(P(t\text{-}Bu)Pr_2)_2$[3].

Relationship between $RhCl_2(PCy_3)_2$ and $RhHCl_2(PCy_3)_2$

$RhHCl_2(PCy_3)_2$ is converted by light into $RhCl_2(PCy_3)_2$, and the former has to be stored in the dark to avoid contamination by the latter. Conversely, the Rh(II)-complexes $RhClX(PCy_3)_2$ are often contaminated by the corresponding Rh(III)-hydrido compounds, but some purification can be accomplished by washing the insoluble Rh(II)-complexes with benzene.

During the reduction of $RhCl_3.3H_2O$ with PCy_3 the initially formed product is $RhCl_2(PCy_3)_2$, contaminated with some $RhHCl_2(PCy_3)_2$; and when the reaction proceeds, relatively more of the latter is formed. We observed that the Rh(II) and the Rh(III)-complexes are formed less contaminated the one with the other, when the method of oxidation of $RhCl(PCy_3)_2$ is used.

Reactions of $RhHCl_2(PCy_3)_2$

Some reactions of $RhHCl_2(PCy_3)_2$ have been studied. CO adds reversibly to $RhHCl_2(PCy_3)_2$, presumably with formation of $RhHCl_2(CO)(PCy_3)_2$ (in benzene ν(Rh-H) at 2100 and ν(CO) at 2020 cm^{-1}) and of a non-identified compound with an absorption at 2070 cm^{-1}. Upon prolonged treatment with CO, $RhCl(CO)(PCy_3)_2$ is formed by elimination of HCl. $RhCl(CO)(PCy_3)_2$ itself forms with HCl only traces of $RhHCl_2(CO)(PCy_3)_2$ which has ν(Rh-H) at 2060 and ν(CO) at 2000 cm^{-1} [16]. This suggests that with the different procedures isomers of $RhHCl_2(CO)(PCy_3)_2$ are formed, which have CO and HCl respectively as labile groups.

The reaction of acetylene, C_2H_2, with $RhHCl_2(PCy_3)_2$ is very slow, and even after 3 days only traces of the vinyl product $Rh(CH{=}CH_2)Cl_2(PCy_3)_2$ (ν(C=C) at 1555 cm^{-1}) could be isolated. With pyridine, a fast and complete conversion could be achieved into the coordinatively saturated 18-electron complex $RhHCl_2(py)(PCy_3)_2$, for which a Rh-H stretching vibration frequency could be detected at 2135 cm^{-1}. This observation can be considered as an additional proof for the presence of a hydride ligand in the starting complex $RhHCl_2(PCy_3)_2$.

Reaction of $RhCl(PCy_3)_2$ with MeI and with $NaBH_4$

The easy formation of Rh(II)-complexes in the oxidation of $RhCl(PCy_3)_2$ with halogens was a motive to investigate whether in the reaction with methyliodide Rh(II)-complexes could be formed in a substantial amount. The reaction, when carried out in benzene, is very fast and $RhMeI_2(PCy_3)_2$ is formed. No Rh(II) could be detected with E.P.R. in the isolated product. The reaction of MeI with a suspension of $RhCl(PCy_3)_2$ in hexane is slow and yields $RhMeClI(PCy_3)_2$. Here too, no Rh(II) was present in the isolated product. Due to the cyclohexyl groups, the methyl group is not unambiguously detected in the PMR and IR spectra, but its

presence is sufficiently proven by the use of CD_3I. The proposed structure of the complexes $RhMeXI(PCy_3)_2$ (X = Cl, I) is square pyramidal with an axial Me, *trans*-phosphines and *trans*-halogens (Fig. 1).

The recent paper on $RhH_2(BH_4)(P(t\text{-}Bu)_2Me)_2$[17] prompts us to report the synthesis of $RhH_2(BH_4)(PCy_3)_2$ from $RhCl(PCy_3)_2$ and an excess of $NaBH_4$. The compound shows in the infrared ν(B-H) near 2400, ν(Rh-H) near 2100 and ν(Rh-H-B) at 1925 cm^{-1}. In the PMR spectrum, the BH_4 protons are dynamically equivalent and appear as a broad resonance centered at τ = 13 ppm at room temperature. The ^1J(Rh-H) of 15 Hz for the terminal hydrides is indicative of an octahedral structure, so we think BH_4 to be a bidentate ligand (Fig. 1). The compound shows the inertness of a coordinatively saturated 18-electron system, and is not able to hydrogenate olefins.

The stability of Rh(II)-complexes with bulky phosphines

The stability of Rh(II)-complexes with bulky phosphines needs some further consideration. The alternatives for a Rh(II)-complex are so numerous that few paramagnetic Rh(II)-complexes yet have been prepared. The role of the bulkiness of the phosphine is to prevent the formation of such alternatives as *tris*-phosphine complexes $RhCl_3(PR_3)_3$ or $RhHCl_2(PR_3)_3$. It then causes the formation of a Rh(II)-complex or of a five-coordinate mono-hydride $RhHCl_2(PR_3)_2$. Discussing the existence of $RhCl_2(PR_3)_2$ then is discussing the non-existence of $RhCl_3(PR_3)_2$ and the relative stability of $RhCl(PR_3)_2$, $RhCl_2(PR_3)_2$ and $RhHCl_2(PR_3)_2$. These four types of complexes belong to classes of compounds with an unfavourable electron configuration and a concomitant small existence range, namely three-coordinate d^8, low spin d^7 and five-coordinate low spin d^6. It seems (*i*) that electronic effects determine the non-existence of $RhCl_3(PR_3)_2$ and (*ii*) steric effects decide about the formation of $RhCl_2(PR_3)_2$ or $RhHCl_2(PR_3)_2$.

(*i*) On the basis of the low polarizability of the halogen and the moderate polarizability of the phosphine ligands, a theoretical order of increasing positive charge on the central metal can be given for the series of known and reported non-existing (n.e.) rhodium-halo phosphine complexes:

$[RhCl_2(PR_3)_2]^-$ (n.e.)[18] < $[RhCl(PR_3)_2]_2$[19] < $RhCl(PR_3)_3$[19] < $RhCl(PR_3)_2$[9] < $RhCl_2(PR_3)_2$ ~ $[RhCl_4(PR_3)_2]^-$[18] < $RhCl_3(PR_3)_3$[20] < $RhCl_3(PR_3)_2$ (n.e.)

That the extremes of the range do not (not yet) exist as isolable complexes is undoubtedly an electronic effect. The low to moderate polarizability of the halogen and the phosphine, and the relatively weak over-all donor properties of the phosphine leave such a high residual positive charge on the $RhCl_3(PR_3)_2$-fragment that this charge should obviously be compensated by the coordination of at least one additional donor ligand. The instability of $RhCl(PCy_3)_2$ has been discussed elsewhere[11]. The stability of $RhCl_2(PCy_3)_2$ in a reduction of $RhCl_3.3H_2O$ with PR_3 or in an oxidation of $RhCl(PR_3)_2$ with Cl_2, as well as the stability of the Rh(II)-complexes towards disproportionation: 2 $RhCl_2(PR_3)_2$ = $RhCl(PR_3)_2$ + $RhCl_3(PR_3)_2$ must then be considered to be of thermodynamic origin, caused by the high energy of the Rh(I) and Rh(III) compounds. That $RhHCl_2(PR_3)_2$ does exists as a five-coordinate d^6-complex but $RhCl_3(PR_3)_2$ not, may be ascribed to the lower electronegativity of the hydrogen compared with the chlorine ligand.

(*ii*) Preference of $RhHCl_2(PR_3)_2$ over $RhHCl_2(PR_3)_3$ seems to be governed largely by steric effects, *e.g.* small phosphines form the *tris*-complex[20], and more bulky phosphines, like $P(t\text{-Bu})R_2$[3], the *bis*-complex. PPh_3 and $P(i\text{-Pr})_3$ have an intermediate position, for these ligands $RhHCl_2(PR_3)_2$ as well as $RhHCl_2(PR_3)_3$ have been reported[13,21]. With the most bulky phosphines, *e.g.* $P(t\text{-Bu}_2R)$, PCy_3 and $P(o\text{-Tol})_3$, $RhCl_2(PR_3)_2$ is preferred over $RhHCl_2(PR_3)_2$; the donor-acceptor properties of the phosphine are clearly of

minor importance in this preference, as both bulky alkyl- and arylphosphines form Rh(II)-complexes.

INTERPRETATION OF THE E.P.R. G-VALUES

The first derivative X-band E.P.R. powder spectra of the undiluted rhodium(II) complexes showed one g-value (g_1) near 4 and two g-values ($g_2 > g_3$) near 1.3 (Table 4 and Fig. 2). Hyperfine splittings could not be observed on the broad lines. The spectra are temperature dependent. In this section we shall derive from the g-values the possible ground states of the Rh(II)-complexes, and the position of the magnetic axes relative to the molecular axes, as far as possible.

The large anisotropy of the g-tensor requires a strong mixing of two or more states. We represent two states $|d_1|$ and $|d_2|$ by the d-orbitals d_1 and d_2 in which the states differ; the modulus signs are used to indicate the states. A mixed state can be written as:

$$\Psi = p\,|d_1| + q\,|d_2| \qquad (p^2 + q^2 = 1)$$

where p is defined as the larger coefficient. Covalency is taken into account by the introduction of a covalency (or-

T A B L E 4

EXPERIMENTAL g-VALUES

	Compound	g_{xx}	g_{yy}	g_{zz}
1	$RhCl_2(PCy_3)_2$*	1.68	4.02	1.33
2	$RhCl_2(PCy_3)_2$	1.58	3.96	1.27
3	$RhClBr(PCy_3)_2$	1.56	4.03	1.20
4	$RhClI(PCy_3)_2$	1.65	4.0	1.18
5	$RhBr_2(PCy_3)_2$	1.55	4.09	1.13
6	$RhCl_2(P(o\text{-Tol})_3)_2$*	1.21	4.32	0.92
7	$RhCl_2(P(o\text{-Tol})_3)_2$**	0.98	4.23	0.8

* at -180°C, other values at room temperature

** broad spectrum, approximate g-values

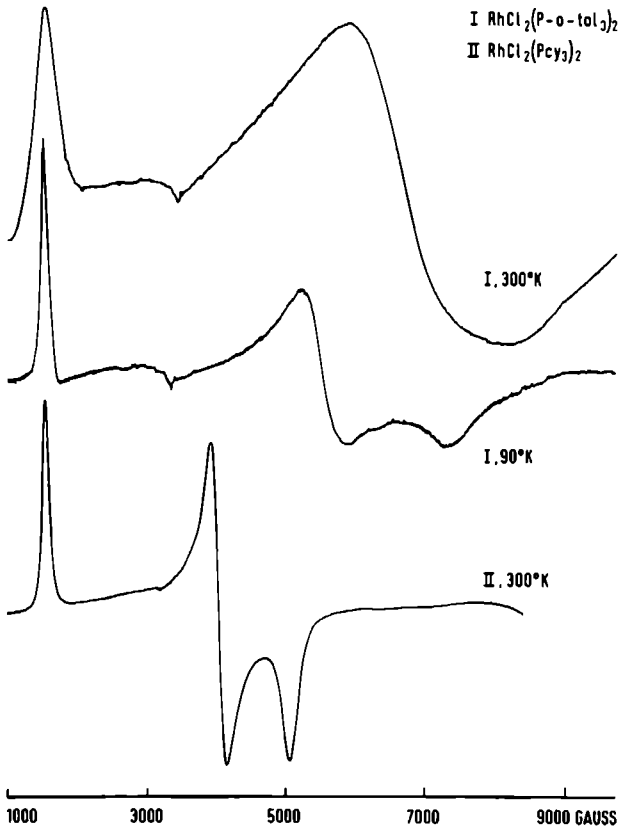

Fig. 2: The X-band E.P.R. powder spectra of $RhCl_2(PR_3)_2$, R = Cyclohexyl, *o*-Tolyl

bital reduction) factor k^{22}. The equations for the g-values derived from Ψ are[23-25]

$$g_{//} = g_e \pm kmpq = g_e \pm kmp(1-p^2)^{\frac{1}{2}}$$

$$g_{\perp} = g_e(1-2q^2) = g_e(2p^2-1)$$

The factor m originates from the L operator and is determined by the actual pair of d-orbitals. The value of m is 0, 4, $4\sqrt{3}$ or 8 and the orbitals to which m refers can be

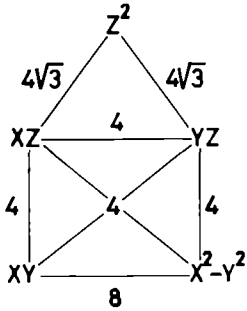

Fig. 3: Value of m as function of the orbital pair (see text).

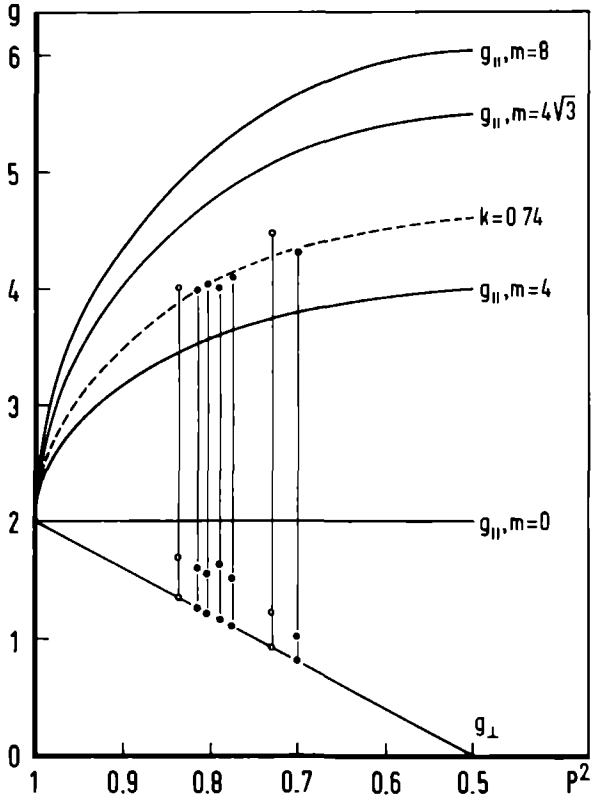

Fig. 4: $g_{//}$ and $g_{\perp}$ as functions of orbital coefficient p, and experimental g-values (o at -180°C; • at room temperature)

read from the "magic pentagon" in Fig. 3 (*cf.* ref. 26).

A graph of $g_{//}$ and $g_{\perp}$ as functions of p^2 for all possible values of m is given in Fig. 4. The graph is valid if the orbitals d_1 and d_2 contain 3 electrons. In this graph, the experimental g-values are also marked. It is obvious that only $4\sqrt{3}$ and 8 are possible values of m; m = 8 refers to the orbitals $d_{x^2-y^2}$ and d_{xy}. It is hard to imagine a four-coordinate d^7-system in which these two orbitals are nearly degenerate, so we reject m = 8 as a possible solution. The remaining possibility, m = $4\sqrt{3}$, corresponds to a mixing of d_{z^2} and d_{xz} (or, what is equivalent by interchange of x and y axes, d_{z^2} and d_{yz}). The result is that there are two possible ground states left for the Rh(II)-complexes; *ca.* 80% $|d_{z^2}|$ + 20% $|d_{xz}|$ and *ca.* 80% $|d_{xz}|$ + 20% $|d_{z^2}|$. Such ground states are found for some four-coordinate Co(II) low spin d^7-systems[27,28], and both of these possible ground states are in agreement with the square planar structure assigned to the Rh(II)-complexes in a preceding section of this paper. Because a square planar *trans*-structure implies D_{2h} as the approximate symmetry of the molecules $RhX_2(PR_3)_2$, it is expected that the magnetic x and y axes are situated along the metal ligand directions. This defines $d_{x^2-y^2}$ as the antibonding, empty orbital. The covalency factor k is found from $g_{//}$ and $g_{\perp}$ in Fig. 4 to be approximately 0.75. This is a realistic value. From the pair of orbitals d_{z^2} and d_{xz}, $g_{//}$ (the g-value near 4) is derived to be g_{yy}. Such an assignment has its precedent in several Co(II)-complexes[27,28].

The assignment of the g_2 and the g_3 values to one of the remaining principal g-values g_{xx} and g_{zz}, and the position of the x and y axes of the g-tensor with respect to axes in the molecule remain to be determined. $g_{\perp}$ (approximately equal to g_3) has given us an approximate value of the mixing percentage of the two orbitals; $g_{//}$ has been used to determine an approximate value of k; the remaining quantity, $g_{xx}-g_{zz}$, may give some further information. For that

TABLE 5

g-EXPRESSIONS FOR d^7 (*cf.* REF. 28)

$d_{x^2-y^2}$ empty, neglected

k isotropic

$|\pm\rangle = a|d_{z^2}| + b|d_{xz}| + ic|d_{yz}| \pm id|d_{xy}|$

a>b, ground state $\|d_{z^2}\|$ (p=a, q=b)
$g_{zz} = g_e(1-2b^2-2c^2) + 4kbc$
$g_{xx} = g_e(1-2b^2-2c^2) - 4\sqrt{3}kac + 4kbd$
$g_{yy} = g_e(1-2c^2-2d^2) - 4\sqrt{3}kab - 4kcd$
$g_{xx}-g_{zz} = 4kbd - 4kc(\sqrt{3}a + b)$

b>a, ground state $\|d_{xz}\|$ (p=b, q=a)
$g_{zz} = g_e(1-2a^2-2d^2) - 4kbc$
$g_{xx} = g_e(1-2a^2-2d^2) + 4\sqrt{3}kac - 4kbd$
$g_{yy} = g_e(1-2c^2-2d^2) - 4\sqrt{3}kab - 4kcd$
$g_{xx}-g_{zz} = 4kc(\sqrt{3}a + b) - 4kbd$

purpose we need more elaborate expressions for the g-values; these are given in Table 5, where the $d_{x^2-y^2}$ orbital has been neglected, because $d_{x^2-y^2}$ does not contribute to $g_{xx}-g_{zz}$, and because it is expected that its contribution to any of the g-values is small.

Under the assumption that spin-orbit coupling is responsible for the mixing of the states, it is readily verified that c and d (which refer to the filled orbitals d_{yz} and d_{xy}) have to be negative if the leading coefficient a (ground state $|d_{z^2}|$) or b (ground state $|d_{xz}|$) is positive.

In both cases g_{xx} is larger than g_{zz}. This permits us to identify with some certainty g_2 with g_{xx} and g_3 with g_{zz}. For square planar d^7 complexes the order $g_{xx}>g_{zz}$ is most usual, although exceptions have been described[28]. Finally, calculations with the experimental g-values and the g-expressions in Table 5 show that one orbital is mainly responsible for the g_{xx}-g_{zz} difference, namely d_{yz} for the ground state $|d_z2|$ (d_{xy} does not normally mix with d_z2 by spin orbit coupling) and d_{xy} for the ground state $|d_{xz}|$ (the influence of d_{yz} is small by a canceling of terms in the factor $(\sqrt{3}a + b)$ at the values a = -0.45, b = 0.9, see Tables 4 and 5). This has led us to calculate approximate coefficients a, b and c for the $|d_z2|$ ground state by putting d = 0, and a, b and d for the $|d_{xz}|$ ground state by putting c = 0 with the aid of the g-expressions in Table 5 and the normalization condition $a^2 + b^2 + c^2 + d^2 = 1$. In addition ΔE_{xz-z^2} and ΔE_{yz-z^2} or ΔE_{xy-xz} have been calculated under the assumption that spin-orbit coupling is responsible for the mixing of the states. The results are given in Table 6. The two solutions correspond to two possibilities for the Kramers doublet of the ground state, a mixture of approximately 80% $|d_z2|$, 20% $|d_{xz}|$ and 1% $|d_{yz}|$, and a mixture of approximately 80% $|d_{xz}|$, 20% $|d_z2|$ and 1% $|d_{xy}|$. As long as additional information (*e.g.* hyperfine couplings, electronic spectra) is not available, no definitive conclusion can be made about the ground state. For both possibilities the variation in the excitation energies ΔE_{yz-z^2} and ΔE_{xy-xz} is in agreement with expectations for the PCy_3 series, based on the spectrochemical series: $ClI \sim Br_2 < ClBr < Cl_2$. However, there is no agreement with the expected order $RhCl_2(PCy_3)_2 < RhCl_2(P(o\text{-}Tol)_3)_2$.

That, by our choice of magnetic axes, the d_{xz} orbital lies higher in energy than d_{yz} permits us to locate tentatively the axis of the highest g-value (y-axis) along the P-Rh-P axis (Fig. 5), as the better π-acceptor properties of the phosphorus ligands compared to the halogen ligands

T A B L E 6

CALCULATED COEFFICIENTS AND ENERGY DIFFERENCES
NUMBERING OF COMPOUNDS AS IN TABLE 4
λ(Rh(II)) = 1235 cm^{-1} (ref. 33)

a. For ground state d_{z^2} (d = 0)

compound	k	a(d_{z^2})	b(d_{xz})	c(d_{yz})	ΔE_{xz-z^2} (cm^{-1})	ΔE_{yz-z^2} (cm^{-1})
1	0.75	0.90	-0.43	-0.094	1050	5050
2	0.71	0.89	-0.45	-0.093	1000	4650
3	0.71	0.88	-0.47	-0.106	850	3900
4	0.71	0.88	-0.47	-0.133	750	2950
5	0.72	0.86	-0.50	-0.131	700	2800
6	0.74	0.84	-0.55	-0.094	550	3800
7	0.70	0.82	-0.57	-0.062	450	5350

b. For ground state d_{xz} (c = 0)

compound	k	b(d_{xz})	a(d_{z^2})	d(d_{xy})	ΔE_{z^2-xz} (cm^{-1})	ΔE_{xy-xz} (cm^{-1})
1	0.80	0.91	-0.41	-0.105	1450	3800
2	0.74	0.90	-0.43	-0.111	1200	3250
3	0.75	0.89	-0.45	-0.124	1150	2850
4	0.75	0.89	-0.45	-0.144	1050	2400
5	0.75	0.88	-0.47	-0.132	1000	2600
6	0.77	0.85	-0.52	-0.096	800	3600
7	0.71	0.84	-0.54	-0.063	650	5350

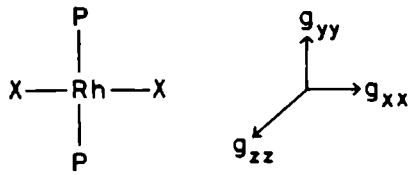

Fig. 5: Magnetic coordinate axis with respect to the molecular axis

stabilize then the d_{yz} orbital with respect to d_{xz}. A single crystal study could decide about this, but is still lacking.

The temperature dependence of the spectra (*cf.* Fig. 2) is partly a consequence of small energy changes, and partly a consequence of a change in the value of k. The slight decrease of k by increasing temperature suggests that a small vibronic contribution to the orbital reduction factor is present (Ham effect[29]).

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CHAPTER IV

INFRARED INTENSITY MEASUREMENTS ON GROUP VIII B,C METAL-ALKYNE COMPLEXES*

H.L.M. VAN GAAL, M.W.M. GRAEF AND A. VAN DER ENT

SUMMARY

The integrated molar absorption coefficients $\bar{A}_{int}$ of the C≡C stretching vibration of the coordinated alkynes of Rh, Ir, Ni and Pt complexes of hexafluorobutyne (HFB), tolane and hexyne have been measured. A relative scale of donor and acceptor interactions in the complexes has been calculated from the measured values of $\bar{A}_{int}$ and $\Delta(\nu^2) = \nu^2$ (free alkyne) - ν^2 (coordinated alkyne). Competitive as well as synergic relations between donor and acceptor bonding has been found. The competitive order of increasing donor and decreasing acceptor bonding has been found for the alkynes HFB → tolane → hexyne. Within the series of complexes of one alkyne, the acceptor bond increases for the metals in the order: Pt(II)(4) < Rh(I)(4) < Ir(I)(4) < Pt(II)(5) < Ni(O)(3) < Pt(O)(3) (coordination number in parentheses) and the donor bonding increases synergically with the acceptor bonding in this series.

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The transition metal-alkyne bond has a dual nature and is usually described by the Dewar, Chatt, Duncanson bonding model[1,2] as being composed of (i) a bond of σ-symmetry, in which the alkyne donates π-electron density to the empty metal orbitals, and (ii) a bond of π-symmetry, in which the antibonding π*-orbitals of the alkyne accept electron density from filled metal orbitals (π-backbonding). In addition, there may be a contribution from the second π- and π*-orbital pair. Both donor and acceptor bonding weaken the coordinated C≡C bond and lower the C≡C stretching vibration frequency.

The C≡C stretching vibration of a coordinated alkyne is accompanied by a change in dipole moment which is perpendicular to the vibrational motion along the metal-alkyne bond. The change in the permanent dipole moment, due to the movements of the nuclear coordinates during the C≡C stretching vibration, is not likely to be of great importance, since this symmetric vibration consists of a motion which is almost perpendicular to the permanent dipole moment. The dipole moment change is therefore mainly determined by the electronic charge migration during the vibration[3]. These changes are calculated to be of opposite sign and of different magnitude for the donor and the acceptor part of the metal-alkyne bond. The infrared intensity of the C≡C stretching vibration, which is proportional to the square of the dipole moment change during the vibration, in combination with the lowering of the frequency of this vibration, gives information on the relative contributions of the donor and acceptor components of the metal-alkyne bond.

Literature data on C≡C stretching vibration intensities of coordinated acetylenes are restricted to incidental qualitative observations[4-6]. Infrared intensity measurements have proved useful in the evaluation of the relative importance of donor and acceptor interactions in complexes of

CO, N_2 and other mono-hapto diatomic ligands[7-11].

In this study, infrared intensity measurements on group VIII B, C transition metal complexes of three different symmetric alkynes are reported. The results are interpreted with the aid of properties of symmetry-adapted alkyne orbitals.

EXPERIMENTAL

Solvents were reagent grade and saturated with argon or nitrogen before use. Metal salts were purchased from Drijfhout, Amsterdam; 2-hexafluorobutyne (HFB) from Pierce; diphenylacetylene (TOL) and 3-hexyne (HEX) from Merck. Hexyne was purified from peroxides over Al_2O_3.

$Pt(PPh_3)_2(HFB)$[12], $Pt(PPh_3)_2(TOL)$[12], $Pt(PPh_3)_2(HEX)$[12], $Pt(CH_3)(HBpz_3)(HFB)$[13] (pz = pyrazolyl, $C_3H_3N_2$), $Ni(PPh_3)_2$-(HFB)[12], $RhCl(PPh_3)_2(HFB)$[14] and $RhCl(PPh_3)_2(TOL)$[15] were prepared as described in the references cited. $IrCl(PPh_3)_2$-(HFB)[16] and $IrCl(PPh_3)_2(TOL)$[17] were prepared from IrCl-$(PPh_3)_2(C_2H_4)$[18] instead of $IrCl(PPh_3)_2(N_2)$. The novel complexes $RhCl(PCy_3)_2(TOL)$ and $RhCl(PCy_3)_2(HEX)$ (Cy = cyclohexyl) were prepared from $RhCl(PCy_3)_2$[19]; full details of their synthesis will be published elsewhere[20].

The purity of the complexes was checked by elemental analyses, carried out by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany, and by infrared and NMR measurements. Analytical data are given in Table 1.

Intensity measurements were carried out under nitrogen or argon in analytical-grade $CHCl_3$ on a Perkin Elmer 225 spectrophotometer, adapted with a linear absorption potentiometer, in 1.0 and 0.5 mm NaCl cells. The cell width was measured by the interference method[21]. The width of the variable reference cell was compensated for the $CHCl_3$ absorption at 2400 cm^{-1} (ref. 22). The slit width of the

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ANALYTICAL DATA

(calculated values in parentheses)

Compound	% C	% H	% Cl	% P	% F
$Pt(PPh_3)_2(HFB)$	55.0	3.7		6.9	12.5
	(55.5)	(3.4)		(7.0)	(12.9)
$Ni(PPh_3)_2(HFB)$	64.3	3.9		8.5	15.2
	(64.6)	(4.1)		(8.2)	(15.4)
$Pt(CH_3)(HBpz_3)(HFB)$	29.6	2.4	14.6 (% N)		17.0
	(28.7)	(2.2)	(14.4)		(19.6)
$IrCl(PPh_3)_2(HFB)$	52.1	3.3			12.5
	(52.8)	(3.3)			(12.5)
$RhCl(PPh_3)_2(HFB)$	58.8	3.9	3.7		13.1
	(58.3)	(4.1)	(4.3)		(13.8)
$Pt(PPh_3)_2(TOL)$	66.5	4.4		7.2	
	(66.9)	(4.5)		(6.9)	
$RhCl(PCy_3)_2(TOL)$	67.7	8.2	3.7		
	(68.5)	(8.8)	(4.0)		
$IrCl(PPh_3)_2(TOL)$	64.7	4.5	3.7	6.8	
	(64.5)	(4.3)	(3.3)	(6.7)	
$RhCl(PPh_3)_2(TOL)$	70.6	4.6	3.7		
	(71.4)	(4.8)	(4.2)		
$Pt(PPh_3)_2(HEX)$	61.2	4.8		8.0	
	(62.9)	(5.0)		(7.8)	
$RhCl(PCy_3)_2(HEX)$	63.7	9.6	3.6	8.3	
	(64.7)	(9.8)	(3.5)	(8.0)	

spectrometer was about 0.3 mm and the spectrum expansion was 4.0 cm^{-1}/cm.

The complexes were measured at three or more different concentrations and they all obeyed Beer's law. The solutions gave a constant intensity for a period of several hours. The intensities were integrated with a calibrated planimeter, and base line correction for phenyl overtones was applied. The width of the base was taken five times the width at half height $(\delta\nu)_{\frac{1}{2}}$[7]. Some complexes showed a shoulder or a double absorption peak, which we attribute to Fermi resonance doubling[23]. In those cases the total intensity of both absorptions has been taken.

RESULTS

The infrared vibration under consideration is acceptably described by a 5-center model of C_{2v}-symmetry, comprising the cental metal, the two acetylenic carbon atoms and the two substituent atom groups (Fig. 1). From the seven fundamental in-plane vibrations, four belong to the A_1 representation. With the aid of tabulated G-matrix elements [24] and estimated force constants[25,26] it is verified that contributions of the lower frequency vibrations to the commonly called C≡C stretching vibration in the 1700-2000 cm^{-1} region do not exceed 10%, so that approximation by a pure C≡C stretching vibration does not introduce large errors.

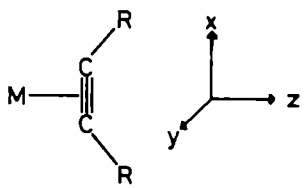

Fig. 1: Coordinate axes

The integrated molar absorption coefficient $\bar{A}_{int}$ is defined as[27]:

$$\bar{A}_{int} = \int \bar{A}\, d\nu = 2.303(1/CL)\int_{band} \log(I_o/I_t)\, d\nu \qquad (1)$$

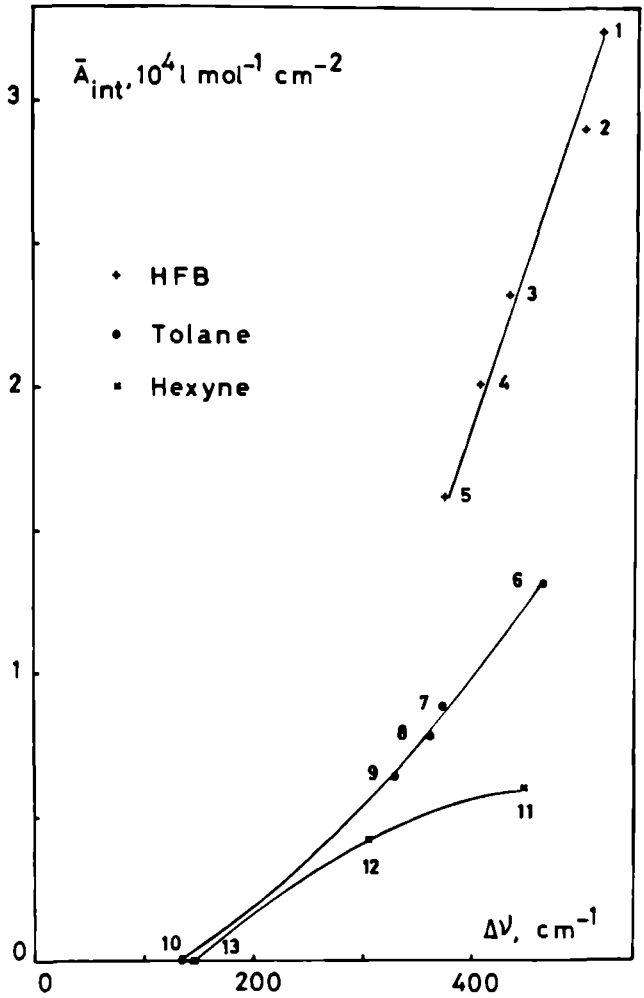

Fig. 2: $\bar{A}_{int}$ versus $\Delta\nu$. Numbering of the complexes as in Table 4.

its dimension is liter.mol^{-1}.cm^{-2}. $\bar{A}$ is the molar absorption coefficient in liter.mol^{-1}.cm^{-1}; C is the concentration in mol.liter^{-1} and L is the cell width in cm. Table 2 gives, together with some other infrared data, the measured values of $\bar{A}_{int}$, with the maximum deviation in parentheses. A plot

TABLE 2: INFRARED INTENSITY DATA AND CALCULATED

Compound	$\nu(C\equiv C)$ cm^{-1}	$\Delta\nu(C\equiv C)$ cm^{-1}	$(\delta\nu)_{\frac{1}{2}}$ cm^{-1}
Hexafluorobutyne[a]	2300		
$Pt(PPh_3)_2(HFB)$	1773	527	22
$Ni(PPh_3)_2(HFB)$	1791	509	19
$Pt(CH_3)(HBpz_3)(HFB)$	1862 1833	438	17 14.5
$IrCl(PPh_3)_2(HFB)$	1889 1903	441	13
$RhCl(PPh_3)_2(HFB)$	1921	379	15
Diphenylacetylene[a]	2222		
$Pt(PPh_3)_2(TOL)$	1742 1768	467	20 20
$RhCl(PCy_3)_2(TOL)$	1847	375	26
$IrCl(PPh_3)_2(TOL)$	1857	365	15
$RhCl(PPh_3)_2(TOL)$	1885 1898	330	19
$[Pt(CH_3)(AsMe_3)_2(TOL)]^{+}$[a,b]	2087	135	-
3-hexyne	2247		
$Pt(PPh_3)_2(HEX)$	1798	449	24
$RhCl(PCy_3)_2(HEX)$	1941 1956sh	306	18
$[Pt(CH_3)(PMe_2Ph)_2(HEX)]^{+}$[a,b]	2101	146	-

[a] In Raman spectrum

[b] Data from ref. 5

$10^{-3}\bar{A}_{max}$ $l.mol^{-1}cm^{-1}$	$10^{-4}x\bar{A}_{int}$ $l.mol^{-1}cm^{-2}$	$(d\mu/dr)_{calc}$ a.u.	$10^{-4}x\Delta(\nu^2)$ cm^{-2}
1.215	3.22(9)	0.81	215
1.150	2.88(8)	0.77	208
0.748 0.402	2.31(7)	0.67	182
0.990 0.547	2.00(6)	0.64	172
0.822	1.61(7)	0.57	160
0.277 0.277	1.31(10)	0.52	186
0.245	0.88(4)	0.42	153
0.387	0.78(5)	0.40	149
0.146 0.171	0.64(2)	0.36	136
ca. 0.0	-	*ca.* 0.0	58
0.191	0.60(4)	0.35	181
0.145	0.42(3)[c]	0.29	128
ca. 0.0	-	*ca.* 0.0	64

[c] $RhCl(PCy_3)_2(CO)$ absorps strongly at 1947 cm^{-1}. A trace of this compound, although not detected in the ^{31}P NMR and IR spectra, may be present. This may increase the measured value of $\bar{A}_{int}$ of $RhCl(PCy_3)_2$(HEX).

of $\bar{A}_{int}$ versus $\Delta\nu = \nu$(free alkyne)- ν(coordinated alkyne) is given in Fig. 2.

The experimental absorption coefficient $\bar{A}_{int}$ is related to molecular quantities by the expression[27]:

$$\bar{A}_{int} = 8\pi^3 N\nu|\mu_{01}|^2/(3hc.1000) \qquad (2a)$$

where N is Avogadro's number; h is Planck's constant; c is the velocity of light, μ_{01} is the transition moment of the vibration, 0 refers the ground state ψ_0 and 1 to the excited state ψ_1. Although the dipole moment μ is not along the carbon-carbon bond direction, the approximation[27]

$$\mu_{01} = (d\mu/dr)_{r=r_o} \langle\psi_0|r|\psi_1\rangle \qquad (2b)$$

still holds. r is the C≡C distance, r_o the equilibrium distance.

The harmonic oscillator approximation[27] for ψ_0 and ψ_1, valid for a stretching vibration, permits evaluation of $\langle\psi_0|r|\psi_1\rangle^2$. This approximation contains a systematic deviation for the complexes, which we assume to be similar for all complexes because of their geometrical similarity, and which then has no consequences for the results.

With the harmonic oscillator approximation, the dipole moment change during the vibration, normalized with respect to the vibrational amplitude, is calculated from eqs. 2a and 2b, in units of the electron charge:

$$d\mu/dr = \pm (1/e) [\bar{A}_{int}.3c^2.1000.m_1m_2/(\pi(m_1+m_2)N^2)]^{\frac{1}{2}} = \pm 0.453\ \bar{A}_{int}^{\frac{1}{2}} \qquad (3)$$

where e is the electron charge in e.s.u. and m_1 and m_2 are the oscillating masses: $m_1 = m_2 = 12$.

Values of $d\mu/dr$, calculated with this formula from the experimental $\bar{A}_{int}$ values, are given in Table 2. This Table also contains values of $\Delta(\nu^2) = \nu^2$(free alkyne)- ν^2(coor-

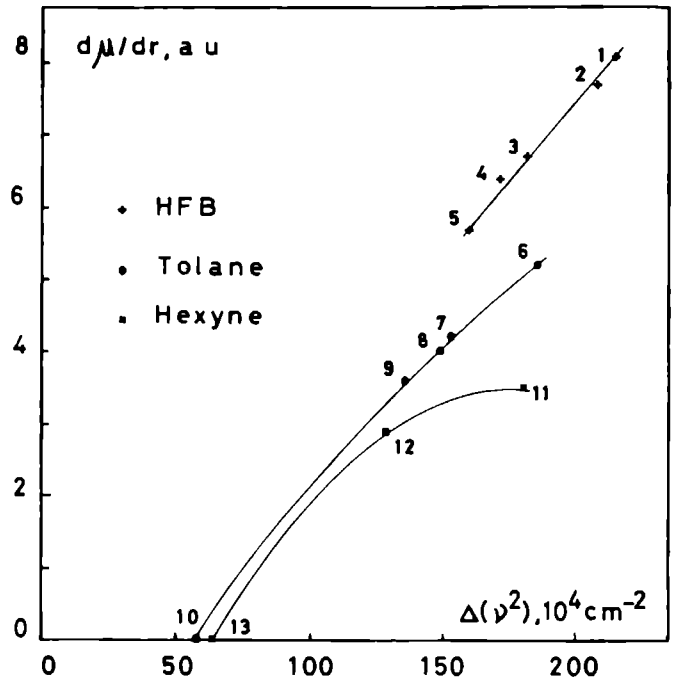

Fig. 3 $[d\mu/dr)_{calc}$ versus $\Delta(\nu^2)$.
Numbering of the complexes as in Table 4.

dinated alkyne), which are related to the force constant and the bond order. A plot of $d\mu/dr$ versus $\Delta(\nu^2)$ is given in Fig. 3.

INTERPRETATION

Symmetry-adapted orbitals

The measured complexes, with the exception of $Pt(CH_3)$-$(HBpz_3)$(HFB), possess C_{2v}-symmetry in solution. The metal-alkyne bond may thus be described by orbital interactions within the four irreducible representations of the C_{2v}-point

TABLE 3

ORBITAL CORRELATIONS FOR THE METAL-ALKYNE FRAGMENT IN C_{2v}-SYMMETRY

Representation	Interaction type	Metal orbitals	Alkyne orbitals
A_1	σ-donor	d_{z^2}, $d_{x^2-y^2}$, s, p_z	σ, π_z
B_2	π-donor	d_{yx}, P_y	π_y
B_1	π-acceptor	d_{xz}, P_x	σ^*, π_z^*
A_2	δ-acceptor	d_{xy}	π_y^*

group (Table 3). For an analysis of $\Delta(\nu^2)$ and of $d\mu/dr$ we make use of the properties of symmetry-adapted orbitals of the alkyne. With ϕ_1^1 and ϕ_2^1 as symmetry-related orbitals of carbon atoms 1 and 2, the acetylenic bonding χ_b^1 and antibonding χ_a^1 orbitals have the form:

$$\chi_b^1 = N_b^1(\phi_1^1 + \phi_2^1) \qquad \chi_a^1 = N_a^1(\phi_1^1 - \phi_2^1) \qquad (4)$$

$$N_b^{1\,2} = (2 + 2S_{CC}^1)^{-1} \qquad N_a^{1\,2} = (2 - 2S_{CC}^1)^{-1} \qquad (5)$$

where $S_{CC}^1 = \langle\phi_1^1|\phi_2^1\rangle$. The normalization constants N_b^1 and N_a^1 differ in the sign of S_{CC}^1, and we shall show that this has far-reaching consequences. The p_π orbitals at a carbon-carbon distance of 1.25 Å have $S_{CC} = 0.33$, which leads to the values $N_\pi^2 = 3/8$ and $N_{\pi^*}^2 = 3/4$, and a ratio $(N_{\pi^*}/N_\pi)^2 = 2$. We take the diagonal term of ϕ_1^1 in the Hamiltonian matrix as a reference: $\langle\phi_1^1|H|\phi_1^1\rangle = 1$. With the use of the Wolfsberg-Helmholz approximation[28] $H_{kl} = \frac{1}{2}KS_{kl}(H_{kk} + H_{ll})$ for

the off-diagonal terms, this results in diagonal terms E_b^i and E_a^i for the χ_b^i and χ_a^i orbitals of:

$$E_b^i = 2(1 + KS_{CC}^i).N_b^{i\,2} \qquad E_a^i = 2(1 - KS_{CC}^i).N_a^{i\,2} \qquad (6)$$

Filled M.O.'s of the metal-alkyne complex take the general form:

$$\psi_{don}^i = C_M^i \chi_M^i + C_b^i \chi_b^i \qquad \psi_{acc}^j = C_m^j \chi_M^j + C_a^j \chi_a^j \qquad (7)$$

ψ_{don}^i and ψ_{acc}^j describe the alkyne-to-metal donor and alkyne-from-metal acceptor interactions respectively. From here on, i refers to filled M.O.'s of the complex containing an alkyne orbital filled in the free alkyne, and j to filled M.O.'s containing an alkyne orbital empty in the free alkyne. Eqs. 4 and 7 combine to give an expression for the coefficients of the carbon atomic orbitals in the filled M.O.'s of the complex:

$$C_1^i = C_2^i = C_b^i N_b^i \qquad C_1^j = C_2^j = C_a^j N_a^j \qquad (8)$$

$\Sigma_i 2(1 - C_b^{i\,2})$ is the amount of charge donated from alkyne orbitals to metal orbitals, and $\Sigma_j 2C_a^{j\,2}$ the amount of charge accepted from metal orbitals into alkyne orbitals. We define a measure of the alkyne-to-metal donor interaction strength as:

$$(don) = \sum_i 2(1 - C_b^{i\,2}) \qquad (9a)$$

and a measure of the alkyne-from-metal acceptor interaction strength as:

$$(acc) = \sum_j 2C_a^{j\,2} \qquad (9b)$$

ν^2 is proportional to the force constant f_{CC} of the CC stretching vibration. f_{CC} is related to the carbon coefficients of the doubly filled M.O.'s by[29,30]:

$$f_{CC} = a \sum_k 2C_1^k C_2^k + b = a \sum_k 2C_1^{k\,2} + b = a\, P_{CC} + b \qquad (10)$$

The summation k runs over all filled M.O.'s; P_{CC} is the carbon-carbon bond order, and a and b are constants. So is a' in:

$$\Delta f_{CC}(:)\ \Delta(\nu^2) = a'\ \Delta P_{CC} \qquad (11)$$

From the various equations, $\Delta(\nu^2)$ is calculated:

$$\Delta(\nu^2) = a' \left[\sum_i 2(1 - c_b^{i\,2}) N_b^{i\,2} + \sum_j 2C_a^{j\,2}\ N_a^{j\,2}\right] \qquad (12)$$

Under the assumption that the contributions of the alkyne π and π^* orbitals to the metal-alkyne interaction dominate those of the σ- and σ^*-orbitals, the substitution of N_b^i by N_π and N_a^j by N_{π^*} is a reasonable simplification for eq. 12 which then becomes by the use of eq. 9 (α is a proportionality constant):

$$\Delta(\nu^2) = \alpha \left[(\text{don}) + (N_{\pi^*}/N_\pi)^2\ (\text{acc})\right] \qquad (13)$$

This equation emphasizes that the acceptor interactions have a greater weight in the lowering of the frequency of the carbon-carbon stretching vibration than the donor interactions, and that this is largely due to the differences in normalization constants ($(N_{\pi^*}/N_\pi)^2 \approx 2$).

The carbon-carbon stretching vibration of the coordinated alkyne belongs to the A_1 representation in C_{2v}-symmetry. Consequently, the dipole moment and its derivative are equal to their component along the M-C_2 axis (z-axis in Fig. 1):

$$\mu = \mu_z = 2e\bar{z} = 2e\left[\sum_i \langle\psi^i_{don}|z|\psi^i_{don}\rangle + \sum_j \langle\psi^j_{acc}|z|\psi^j_{acc}\rangle\right] = \sum_i \mu_i + \sum_j \mu_j \qquad (14)$$

with i and j as formerly defined. On the basis of the atomic orbitals, the overlaps S_{kl} are the only geometry-dependent quantities and thus:

$$d\mu_i/dr = \sum_{k,l} (\partial\mu_i/\partial S_{kl})(dS_{kl}/dr) \qquad (15)$$

and similarly for $d\mu_j/dr$. On the basis of the symmetry-adapted orbitals the geometry-dependent quantities are:

$$S^{kl}_{Mb} = \langle\chi^k_M|\chi^l_b\rangle;\ S^{mn}_{Ma} = \langle\chi^m_M|\chi^n_a\rangle;\ E^l_b \text{ and } E^n_a$$

(where E^l_b and E^n_a are functions of S^l_{CC} and S^n_{CC} respectively) and 15 can be rewritten as:

$$d\mu_i/dr = \sum_l (\partial\mu_i/\partial E^l_b)(dE^l_b/dS^l_{CC})(dS^l_{CC}/dr) + \sum_{k,l} (\partial\mu_i/\partial S^{kl}_{Mb})(dS^{kl}_{Mb}/dr) \qquad (16)$$

and similarly for $d\mu_j/dr$. Eq. 16 states that the dipole moment change during the vibration arises from a change in the energy of the alkyne orbitals and a change in the metal-alkyne overlap. Approximate calculations with the use of

Mulliken's expression[31] $\mu_i = C_M^{i\,2} - C_b^{i\,2}$ reveal that the second group of terms in eq. 16 is always about 10% of, and has the same sign as the first group of terms. Under the assumption that the contributions of the alkyne π- and π^*-orbitals to the metal-alkyne interaction dominate over those of the σ- and σ^*-orbitals, one E-term remains in each representation and eq. 16 reduces to:

$$d\mu_i/dr \simeq (\partial\mu_i/\partial E_b^i)(dE_b^i/dS_{CC}^i)(dS_{CC}^i/dr) \qquad (17)$$

and similarly for $d\mu_j/dr$. A slightly different but comparable expression is given in ref. 11. The result, expressed in eq. 17, is that the dominant contribution to the dipole moment change during the vibration originates from the change in energy of the alkyne orbitals caused by the change of the carbon-carbon distance. $\partial\mu_i/\partial E_b^i$ and $\partial\mu_j/\partial E_a^j$ are independent of the geometry. In the parametrized calculations, it turned out that they were reasonably porportional to $1 - C_b^{i\,2}$ and $C_a^{j\,2}$ with the same proportionality constant k:

$$\partial\mu_i/\partial E_b^i \simeq k(1 - C_b^{i\,2}) \qquad \partial\mu_j/\partial E_a^j \simeq kC_a^{j\,2} \qquad (18)$$

From eqs. 5 and 6 it is calculated that:

$$dE_b^i/dS_{CC}^i = 4(K-1)N_b^{\,4} = 4(K-1)N_\pi^{\,4}$$

$$dE_a^j/dS_{CC}^j = 4(1-K)N_a^{\,4} = 4(1-K)N_{\pi^*}^{\,4} \qquad (19)$$

For all π- and π^*-orbitals $S_{CC}^i = S_{CC}^j = S_{CC}$. Substitution of 18 and 19 in 17 leads, after summation over the four irreducible representations, to the simplified expression for $d\mu/dr$:

$$d\mu/dr \simeq 4k(K-1)N_\pi^{\,4}(dS_{CC}/dr)\left[\sum_i (1-C_b^{i\,2}) - (N_{\pi^*}/N_\pi)^4 \sum_j C_a^{j\,2}\right] \qquad (20)$$

With the substitutions 9a and 9b and β as a proportionality constant, we get the expression:

$$d\mu/dr \approx \beta[(don) - (N_{\pi^*}/N_{\pi})^4(acc)] \qquad (21)$$

This expression shows that the ratio between the contributions of (don) and (acc) to $d\mu/dr$ is unaffected by the value of the Wolfsberg-Helmholz parameter K, although according to eq. 20 $d\mu/dr$ itself is strongly dependent on this parameter.

Eq. 21 emphasizes that the acceptor interactions have an about four times greater weight in the dipole moment change during the carbon-carbon stretching vibration than the donor interactions, and that this is determined by the differences in normalization constants.

A scale of donor and acceptor interactions

Equations 13 and 21 permit an evaluation of the measured frequencies and intensities in a relative scale of donor and acceptor interaction strengths. For the elimination of the proportionality constants α and β, we have arbitrarily chosen the donor and acceptor interaction strengths of $Pt(PPh_3)_2(HFB)$ (the complex with the largest frequency difference and the largest intensity) to be equal, and to have the reference value 1. With the use of these reference values and of the value $(N_{\pi^*}/N_{\pi})^2 = 2$, a relative scale of donor and acceptor interaction strengths is calculated from the measured values (Table 4). The results are presented graphically in Fig. 4. Because of the simplifications involved in the model and because of the necessarily arbitrary ratio of the reference values, these scales should be considered separately. The acceptor scale is rather insensitive to the chosen acceptor to donor ratio in the reference complex, because of the larger coefficients

TABLE 4

CALCULATED RELATIVE DONOR AND ACCEPTOR INTERACTION STRENGTHS IN ALKYNE COMPLEXES

	Compound	(acc)	(don)
1	$Pt(PPh_3)_2(HFB)$	1[a]	1[a]
2	$Ni(PPh_3)_2(HFB)$	0.96	0.98
3	$Pt(CH_3)(HBpz_3)(HFB)$	0.84	0.87
4	$IrCl(PPh_3)_2(HFB)$	0.80	0.81
5	$RhCl(PPh_3)_2(HFB)$	0.72	0.78
6	$Pt(PPh_3)_2(TOL)$	0.75	1.08
7	$RhCl(PCy_3)_2(TOL)$	0.61	0.90
8	$IrCl(PPh_3)_2(TOL)$	0.59	0.89
9	$RhCl(PPh_3)_2(TOL)$	0.54	0.82
10	$[Pt(CH_3)(AsMe_3)_2(TOL)]^+$	0.14	0.54
11	$Pt(PPh_3)_2(HEX)$	0.64	1.24
12	$RhCl(PCy_3)_2(HEX)$	0.48	0.84
13	$[Pt(CH_3)(PMe_2PH)(HEX)]^+$	0.15	0.59

[a] Taken as reference value

of (acc) than of (don) in eqs. 13 and 21; however, this is not so for the donor scale. The donor scale only allows comparison of complexes with the same alkyne ligand; for complexes with the same metal substrate but with different alkynes the donor scale only indicates trends.

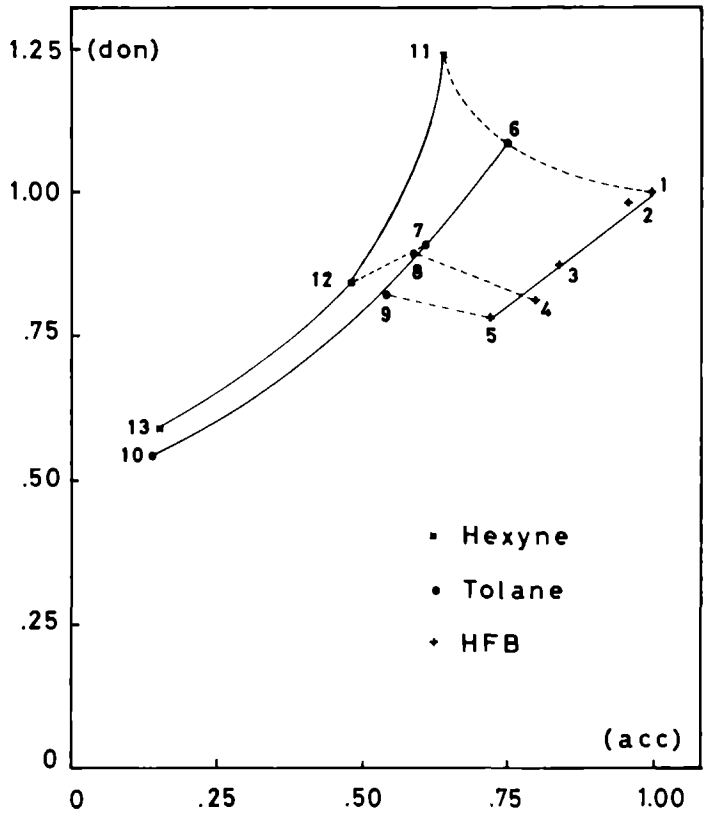

Fig. 4: (don) versus (acc) in metal-alkyne complexes. Numbering of the complexes as in Table 4.

DISCUSSION

With respect to acceptor interactions, the complexes behave largely as expected, but with respect to donor interactions there are some unexpected trends. Electronegative substituents on the alkyne should increase its acceptor properties at the expense of its donor properties[12,32] and this is found to be so: the order of decreasing acceptor and increasing donor interaction strength, keeping the same

metal, is (dashed lines in Fig. 4):

hexafluorobutyne → tolane → hexyne

The metal centers show the expected order for backbonding, but not for bonding. Three-coordinate Pt(0) is the better and four-coordinate Pt(II) the less backbonding metal. In agreement with the increase of metal basicity going down a group[33], Pt(0) is a better backbonding metal than Ni(0), and Ir(I) than Rh(I) when the same ligands are present. Also, Rh(I) is a better backbonding metal with PCy_3 than with the less basic PPh_3 as a ligand. The position of five-coordinate Pt(II) on the scale confirms the aptness of trigonal bipyramidal d^8-complexes for backbonding towards ligands in the equatorial plane[34] and is a further justification of the division of metal olefin and acetylene complexes into class S (square planar + octahedral) and class T (trigonal + trigonal bipyramidal complexes) as given by Hartley[35]. It is unexpected that, keeping the same alkyne and changing the metal center (full lines in Fig. 4), the donor interactions increase smoothly with the acceptor interactions and not at their expense. Schematically, the results can be presented as follows:

$d^8(4)$, M(II)	$d^8(4)$, M(I)	$d^8(5)$, M(II)	$d^{10}(3)$, M(O)
Pt(II)	Rh(I)		
	Ir(I)	Pt(II)	Ni(O)
			Pt(O)

↓ increasing acceptor and donor bonding

This correlated increase of donor and acceptor interactions, keeping the same alkyne and changing the metal, needs further comment. It is tempting to ascribe this to the synergic mechanism, which can be described as follows: the mere presence of a π-bond strengthens the σ-bond by shortening the bond distance, and because the π-bond is an acceptor bond, this effect is reinforced by an increased positive charge on the metal and an increased charge on the ligand, which makes the metal-ligand combination more apt for σ-bonding; a similar influence of the σ-bond on the π-bond is possible[36]. In our results, the donor interactions follow the acceptor interactions. Within the scope of the synergic mechanism, only if it is assumed that the influence of the π-bond on the σ-bond dominates the influence of the σ-bond on the π-bond, can these results be interpreted. The expected decrease in donor bonding going from hexyne to tolane to hexafluorobutyne should then be reduced but not wiped out by the increased acceptor bonding.

That changes in the acceptor bond dominate changes in the total metal-alkyne bond supports the results of our theoretical analysis that the acceptor bond has the greater influence in the frequency shift and the intensity of the carbon-carbon stretching vibration. The common assumption in the discussion of the metal-alkene and metal-alkyne bond of group VIII metals, to emphasize the influence of changes in the π-character of these bonds on the various bonding characteristics, finds here its justification.

This does, however, not imply that the acceptor bond should be stronger than the donor bond. Although in Table 4 the acceptor-to-donor ratio depends on the chosen reference, this is not so for the four-coordinate Pt(II)-complexes, where the zero intensity of the C≡C stretching vibration gives directly from eq. 21 the ratio (acc)/(don) = 20/80. It is interesting to compare this with the results of some molecular orbital calculations on $[PtCl_3(C_2H_4)]^+$, a comparable square planar Pt(II)-alkene complex. In the calcula-

tions are given the metal-alkyne donor and acceptor overlap populations rather than the changes in alkyne orbital occupation, used by us and defined in eq. 9, but these quantities are readily comparable measures for the metal-h[2] ligand interaction. An early extended Hückel calculation[37] and a CNDO-type calculation[38] gave almost equal π- and σ-overlap populations, but a later extended Hückel calculation[39] and a recent SCF-Xα-SW calculation[40] gave a π- to σ-overlap population ratio of about 31/69 and 25/75 respectively. Our results agree qualitatively with the latter two calculations, and confirm that for four-coordinate Pt(II) π-backbonding is relatively weak.

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CHAPTER V

COORDINATION GEOMETRY AND π-ACID BONDING

H.L.M. VAN GAAL

SUMMARY

The various orbital correlations in transition metal π-acid complexes have been analysed. It has been found that the mutual influence of a σ-donor and π-acceptor ligand, exerted through the metal center, depends on the coordination geometry. It is concluded that (i) a π-acid ligand tends to bend *cis*-ligands away, increasing the bond angle between itself and the *cis*-ligand, and (ii) an order of π-backbonding ability of the central metal as a function of coordination geometry is: trigonal d^{10} ∿ trigonal bipyramidal d^8 (equatorial π-acid) > tetrahedral d^{10} > octahedral d^6 ∿ trigonal bipyramidal d^8 (axial π-acid) > square planar d^8. From the literature, experimental data are given which support the conclusions.

INTRODUCTION

In the Dewar-Chatt-Duncanson model[1,2] of the bonding between a transition metal center and a π-acid (end-on coordinated like CO and N_2, or side-on like olefins, dioxygen and acetylenes), the bond consists of a part with σ-symmetry, in which electron density is given from symmetry-adapted ligand orbitals to the metal, and a part with π-symmetry, in which electron density is backdonated from the metal to the π-acid.

In Chapters II and IV of this thesis we noted that two major factors influence the strength of the interaction be-

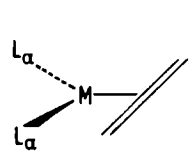
tween the metal center and the π-acid: (i) the electron density brought about at the metal center by its formal valence and by the various other ligands present on the metal, and (ii) the coordination geometry around the central metal in combination with the d^n-configuration. In this chapter, this latter factor is analysed by considering the differences in orbital interactions existing for different coordination geometries. The scope of this analysis is the mutual influence between a π-acid ligand and ligands of mainly σ-donor character in d^6-, d^8- and d^{10}-complexes.

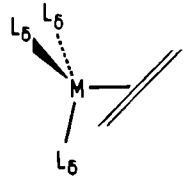
GEOMETRY AND ORBITAL CORRELATIONS

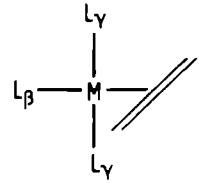
For several coordination numbers the ground state stereochemistry of d^6-, d^8- and d^{10}-complexes with h^2-ligands is well known from X-Ray data (ref. 3-6 and Table 3) and molecular orbital calculations[7,8]. Generally, the same stereochemistry around the metal is found, when an end-on instead of a side-on π-acid is present. In Fig. 1 the various stereochemical situations are given together with the definition of the coordinate axes and the indices α to δ of symmetry-related ligands. The π-acid is represented as a side-on coordinated ligand for convenience.

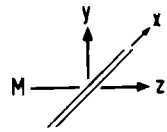
We describe the more important orbital correlations *starting from the local C_{2v}-symmetry of a $M(C_2)$-fragment*. In Table 1, the distribution of the orbitals of the π-acid and the metal over the various irreducible representations within C_{2v}-symmetry is given. The α-, β- and γ-ligand orbital combinations are given in Table 2. The effects of the α-, β- and γ-ligands on the local bond between a metal and a π-acid in the given position can be read from the Tables 1 and 2 in combination with Fig. 1. This is directly possible for square planar, octahedral and trigonal geometry as well as for trigonal bipyramidal geometry with the π-acid on an equatorial position. The influence of ligands in tetrahedral

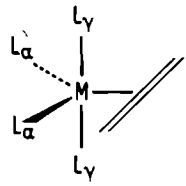
d^{10}(3) trigonal d^{10}(4) tetrahedral d^{8}(4) square planar

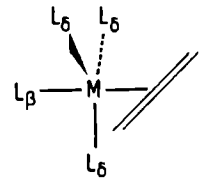


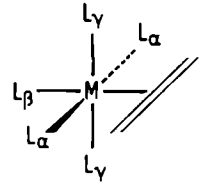












d^{8}(5) TBP_{eq}* d^{8}(5) TBP_{ax}* d^{6}(6) octahedral

* see text

complexes and trigonal bipyramidal complexes with the π-acid on an axial position (δ-ligands) cannot be treated rigorously in terms of symmetry-separated interactions, but their influence on the local M-(π-acid) bond can be readily compared with the influence in other geometries by overlap-considerations.

For end-on π-acids both B_1 and B_2 M.O.'s contribute to π-acceptor bonding, for side-on π-acids only the B_1 M.O.'s are relevant. With the B_1 representation, the π-bonding

T A B L E 1

SYMMETRY ADAPTED ORBITALS, C_{2v}-SYMMETRY, OF LOCAL M-(π-ACID) FRAGMENT

Representation + interaction symmetry	Symmetry adapted orbitals[a]				
	CO, N_2	C_2R_4	C_2R_2	O_2	metal
A_1, σ	$\underline{n}$	$\underline{\sigma}, \underline{\pi}_z$	$\underline{\sigma}, \underline{\pi}_z$	$\underline{\sigma}, \underline{\pi}_z$	$d_{x^2-y^2}, d_{z^2}, s, p_z$[b]
B_1, $\pi_{//}$	π_x^*	σ^*, π_z^*	σ^*, π_z^*	σ^*, π_z^*	$\underline{d}_{xz}$, P_x
B_2, $\pi_\perp$	π_y^*		$\underline{\pi}_y$	$\underline{\pi}_y$	$\underline{d}_{yz}$, P_y
A_2, δ			π_y^*	$\underline{\pi}_y^*$	$\underline{d}_{xy}$

a) Filled orbitals underlined; the symmetry adapted orbitals of the π-acid are indicated by the symbols used for the molecular orbitals of the free molecule;

b) The metal-orbitals in the A_1-representation are either filled or used in σ-bonding.

T A B L E 2

ORBITAL COMBINATIONS FOR LIGANDS L

Ligands (fig. 1)	σ-orbitals	π-orbitals
2 L_α	$A_1 + B_1$	$A_1 + B_1 + B_2 + A_2$
L_β	A_1	$B_1 + B_2$
2 L_γ	$A_1 + B_2$	$A_1 + B_1 + B_2 + A_2$

between the metal and the π-acid is accomplished by a filled metal d_{xz}-p_x hybrid, directed towards the empty orbitals of the π-acid, and the σ-bonding with suitably situated other ligands is accomplished by an empty metal p_x-d_{xz} hybrid, directed away from the π-acid. Both π-bonding to the π-acid ligand and σ-bonding to the other ligands are improved by a better energy matching of the metal and ligand orbitals. A suitable orientation of the α-ligands with respect to the π-acid (suitable bond angles L_α-M-(π-acid), Fig. 1) may increase the p_x-character of the filled hybrid, and the d_{xz}-character of the empty hybrid. The results are a better energy matching between the filled hybrid and the acceptor orbitals of the π-acid on the one hand, and a better energy matching of the empty hybrid with α-ligand σ-orbitals on the other. This results in (i) an influence of the presence of a π-acid ligand on the bond angles at the metal, and (ii) and influence of the coordination geometry on the π-acceptor ability of the metal. A participation of the σ-orbitals of α-type ligands in the molecular orbitals which are responsible for π-backbonding has been established recently by Norman in molecular orbital calculations on $Pt(PH_3)_2(O_2)$[9] and by Rösch and Hoffmann in calculations on $Ni(C_2H_4)_3$[10].

THE INFLUENCE OF π-ACIDS ON BOND ANGLES

In trigonal d^{10}-complexes and in trigonal bipyramidal d^8-complexes with the π-acid equatorially situated, L_α σ-orbitals have a fairly good overlap with the metal d_{xz} orbital. A reduction of the bond angle L_α-M-L_α below the theoretical value of 120° ameliorates the overlap with the metal d_{xz} orbital and is quite commonly found. A few representative examples are given in Table 3. In octahedral complexes the L_α σ-orbitals overlap with the metal p_x orbital, and only by distortions can a small amount of metal d_{xz}-L_α σ-orbital overlap be gained (see Fig. 1). Such a distortion is

T A B L E 3

SELECTED BOND ANGLES IN SOME π-ACID COMPLEXES

Configuration[a]	Compound	Angle	Degree	Ref.
	Ideal geometry	L_α-M-L_α	120	
d^{10}(3)	$Ni(PPh_3)_2(C_2H_4)$	P-Ni-P	112	11
	$Pt(PPh_3)_2(C_2Ph_2)$	P-Pt-P	102	12
	$Pt(PPh_3)_2(CS_2)$	P-Pt-P	107	13
d^8(5)	$IrBr(CO)(PPh_3)_2[C_2(CN)_4]$	P-Ir-P	110.4	14
equat. π-acid	$Ir(diphos)_2(S_2)$	P-Ir-P	98.5	15
	$Fe(CO)_4(CH_2{=}CHCN)$	OC-Fe-CO	108.1	16
	Ideal geometry	L_β-M-$L_{\alpha,\gamma,\delta}$	90	Ref.
d^8(5)	$CoHN_2(PPh_3)_3$	H-Co-P	82*	17
axial π-acid	$Co(SiX_3)(CO)_4$, various X	Si-Co-CO	81-86	18-20
	$IrCH_3(1\text{-}5C_8H_{12})(PR_3)_2$,	H_3C-Ir-P	84-87	21
	various R	H_3C-Ir-(C=C)	83-85	
	$IrCl(C_2H_4)_4$	Cl-Ir-(C=C)	85	22
d^6(6)	$RuCl_2(C_7H_8)(C_6H_5NH_2)_2$	½Cl-Ru-Cl	78.3	23
	$Mn(CO)_5$ X, various X	X-Mn-CO	82.9-87.8	24

a) $d^n(m)$: m = coordination number

* mean of six angles from two crystallographic sites

found in the structure of $RuCl_2(NH_2C_6H_5)_2$(norbornadiene)[23], where the angle L_α-M-L_α is 156.5°, and is also present in complexes of the type $MnX(CO)_5$[24] (Table 3). Trigonal bipyramidal complexes with the π-acid axially situated may be treated in an analogous way. The equatorial ligand σ-orbitals overlap with the metal p_x and p_y orbitals, and by tilting the metal out of the equatorial plane towards the axial π-ligand, some overlap of equatorial ligand σ-orbitals with the metal d_{xz} and d_{yz} is gained. This tilting is a feature often found in TBP complexes with an axial π-acid (Table 3).

The general conclusion may be formulated that: *a π-acid ligand tends to bend cis-ligands away, increasing the bond angle between itself and the cis-ligand* (for a side-on coordinating π-acid this is valid only for the in-plane *cis*-ligands). Experimental support for this conclusion is given in Table 3.

AN ORDER OF π-BACKBONDING ABILITY

The best overlap of L_α σ-orbitals with the metal d_{xz} orbital is found in trigonal d^{10}-complexes and in trigonal bipyramidal d^8-complexes with the π-acid equatorially situated. These geometries give the metal the greatest backbonding ability. Next to them stands the tetrahedral d^{10}-geometry, which has L_α σ-orbitals. These have a better overlap with the metal d_{xz} orbital than the L_α σ-orbitals in octahedral d^6-geometry and than the L_α σ-orbitals in trigonal bipyramidal d^8-complexes with an axial π-acid. The least apt for π-backbonding turns out to be the square planar d^8-geometry. This leads us to the following conclusion: *An order of π-backbonding ability of the central metal as a function of coordination geometry is: trigonal* $d^{10} \sim TBP_{equatorial}\ d^8 >$ *tetrahedral* $d^{10} >$ *octahedral* $d^6 \sim TBP_{axial}\ d^8 >$ *square planar* d^8. Experimental data support the given order, and will be discussed below. This orbital correlation analysis gives a ra-

tionale to Hartley's division of metal-alkene and metal-alkyne complexes into Class T (Trigonal and trigonal bipyramidal) complexes and Class S (Square planar and octahedral complexes[3,25]). One type of data Hartley used for his division concerned the ease of olefin rotation. Square planar and octahedral olefin complexes were characterised by a high rate of olefin rotation. In our model, this is explained by both a weak π-backbond in the ground state and a stabilisation of the transition state by the presence of σ-type ligands in the transition state geometry, after 90° rotation of the olefin. M.O. calculations on the barrier of olefin rotation show that there are two energy minima in square planar d^8-complexes, one for the ground state and one after 90° rotation of the olefin, but that the second minimum is absent in trigonal d^{10}-complexes[7]. Also, the higher rate of rotation of axial than of equatorial ligands in $IrCl(C_2H_4)_4$[26] is in agreement with the predictions based on our model.

Other support comes from infrared data. Both for end-on and for side-on AB π-acids, the AB stretching vibration frequency shifts on coordination. The shift of the frequency indicates the change of the AB bond order and can qualitatively be used as a measure of the M(AB) interaction.

A series of infrared data of hexafluorobutyne (HFB) complexes and a few selected infrared data of dioxygen, diphenylacetylene, allene, tetrafluoroethylene, carbonyl and dinitrogen complexes are shown in Tables 4 and 5, respectively. These data reveal a clear relationship between coordination geometry and π-acid bonding ability of the central metal, in addition to the influence of electron density changes.

Within the series of five-coordinate d^8-complexes, a correlation exists, as expected, between the metal electron density and the HFB stretching vibration frequency (Table 4). It turns out that the influence of the coordination geometry is comparable with the influence of the electron density. This can be seen from the low position of the infrared frequencies of Pt(II) five-coordinate complexes relative to

TABLE 4

$\nu(C\equiv C)$, cm^{-1} OF MONONUCLEAR HEXAFLUOROBUTYNE (HFB) COMPLEXES OF GROUP VIII METALS

Configuration[a]	Compound	$\nu(C\equiv C)$	Ref.
$d^8(4)$	free HFB	2300	
M(I)	$RhCl(PPh_3)_2HFB$	1917	29
	$RhCl(PhHC{=}CHC{=}NPh)_2HFB$	1910	30
	$IrCl(PPh_3)_2HFB$	1885	31
$d^8(5)$	$Pt(CH_3)X(YMe_3)_2HFB$		
M(II)	X = Cl, Br; Y = P, As, Sb	1840-1865	32
	$Pt(CH_3)(HBpz_3)HFB$[b]	1843	33
	$Pt(CH_3)(Bpz_4)HFB$[b]	1861,1833	33
M(I)	$[IrCl(C_8H_{12})HFB]_2$[b]	1860	34
	$[Ir(P(OMe)_3)_4HFB]^+$	1833	35
	$RhCl(SbPh_3)_3HFB$	1825	36
	$IrCl(CO)(PPh_3)_2HFB$	1773	37
	$[Ir(CO)(PPh_3)_2(py)HFB]^+$[b]	1768	38
	$Ir(-C(CF_3){=}CHCF_3)(CO)(PPh_3)_2HFB$	1742	39
	$IrCl(PPh_3)_3HFB$	1735	31
	$IrCl(CO)(PPh_2Me)_2HFB$	1700	31
M(0)	$Os(CO)_2(P(OMe)_3)_2HFB$	1753	40
	$Ru(NO)Cl(PPh_3)_2HFB$	1742	41
$d^{10}(3)$	$Ni(CO)_2HFB$	1905	42
M(0)	$Ni(CO)(PPh_3)_2HFB$	1852	42
	$Ni(CN(t\text{-}Bu))_2HFB$	1848	42
	$Ni(C_8H_{12})HFB$[b]	1846	42
	$Ni(PPh_3)_2HFB$	1790	43
	$Pd(PR_3)_2HFB$	1795-1838	43,44
	$Pt(PR_3)_2HFB$	1758-1775	43-46

a) $d^n(m)$: m = coordination number;

b) pz = pyrazolyl, C_8H_{12} = cyclo-octadiene, py = pyridine

TABLE 5

INFRARED DATA OF SELECTED 3-, 4- AND 5-COORDINATE GROUP VIII COMPLEXES OF π-ACIDS, cm^{-1}

Compound[a]		Vibration	Frequency	Ref.
$RhX(PCy_3)_2(O_2)$	$d^8 4$	$\nu(O=O)$	987-994	47
$MX(PR_3)_2(ligand)(O_2)$ (M=Rh,Ir)	$d^8 5$		832-880	48
$M(PR_3)_2(O_2)$ (M=Pd,Pt)	$d^{10} 3$		830-875	48
$PtCl(acac)(C_2Ph_2)$	$d^8 4$	$\nu(C\equiv C)$	1990	49
$MCl(PR_3)_2(C_2Ph_2)$ (M=Rh,Ir)	$d^8 4$		1847-1916	28,50
$Pt(CH_3)(RBpz_3)(C_2Ph_2)$ (R=H,pz)	$d^8 5$		1818-1816	33
$M(PR_3)_2(C_2Ph_2)$ (M=Ni,Pt)	$d^{10} 3$		1800-1750	28,43
$[Pt(CH_3)(PPhMe_2)_2(C_3H_4)]^+$	$d^8 4$	$\nu_{as}(C=C=C)$	1850	51
$MX(PPh_3)_2(C_3H_4)$ (M=Rh,Ir)	$d^8 4$		1730-1719	52,53
$Pt(CH_3)(HBpz_3)(C_3Me_4)$	$d^8 5$		1720	54
$[Ir(diphos)_2(C_3H_4)]^+$	$d^8 5$		1640	55
$Pt(PPh_3)_2(C_3H_4)$	$d^{10} 3$		1680	55
$Ir(acac)(C_2H_4)(C_2F_4)$	$d^8 4$	$\nu(F_2C=CF_2)$	1497	56
$Ir(acac)(py)(C_2H_4)(C_2F_4)$	$d^8 5$		1385	56
$[Rh(PR_3)_3(CO)]^+$	$d^8 4$	$\nu(C\equiv O)$	2010	57
$[Ir(PR_3)(AsR_3)_2(CO)]^+$	$d^8 4$		2030-2042	58
$MCl(PR_3)(ER_3)_2(CO)$ (M=Rh,Ir;E=P,As)	$d^8 5$		1907-1925	59
$MX(PR_3)_2(N_2)$ (M=Rh,Ir)	$d^8 4$	$\nu(N\equiv N)$	2050-2150	47,60
$Ru(PPh_3)_3(N_2)$	$d^8 4$		2115	61
$Ni(PEt_3)_3(N_2)$	$d^{10} 4$		2074	62
$Ni(PCy_3)_2(N_2)$	$d^{10} 3$		2028	63

a) X = anionic ligand, Cy = cyclohexyl, R = aryl or alkyl, acac = acetylacetonato, pz = pyrazolyl, diphos = bis(diphenylphosphino)ethane.

Rh(I) and Ir(I) four-coordinate complexes. There are reports [27,28] that five-coordinate Pt(II) alkyne complexes resemble more the three-coordinate Pt(0) than the four-coordinate Pt-(II) alkyne complexes with respect to structure, bonding and reactivity.

For d^8-complexes, an increase of the coordination number from four to five is for a host of π-acid ligands accompanied by a decrease in ligand stretching vibration frequency of the π-acid (Table 5). In contrast, in Ni(0) d^{10}-dinitrogen complexes ν(N≡N) increases when the coordination number decreases from three to four (Table 5). These facts support the backbonding ability orders square planar < $TBP_{equatorial}$ and tetrahedral < trigonal.

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SUMMARY

Rhodium compounds with phosphines as ligands are active catalysts for a manyfold of organic reactions. The organic reagents may be temporarily coordinated to the rhodium during the catalytic process. In order to be able to bind an organic reactant the metal center needs a vacant coordination site. This thesis describes a synthetic study of the stabilisation of intermediates in catalytic processes by the use of the bulky ligand tricyclohexylphosphine, and spectroscopic studies of various types of intermediates.

By the use of the bulky tricyclohexylphosphine are synthesized for the first time rhodium(I) complexes with the low coordination number of three. For this purpose the novel compound $[RhF(cyclooctene)_2]_n$ has been very useful. The proof of the three-coordination has been given with ^{31}P nuclear magnetic resonance. The three-coordinate rhodium(I) compounds give stable addition complexes with molecular nitrogen and molecular oxygen, as well as with a variety of unsaturated organic molecules: CO, C_2H_4, acetylenes, CS_2, COS, RNCS, RNCO, RNCNR, SO_2 and PhNO. Some of these compounds are peculiar by the four-coordination of the rhodium, others by the new bonding mode of the organic molecule (Chapter II).

The three-coordinate rhodium(I) complexes have been oxidized by the addition of hydrogen, hydrogeneous halides, halogens and methyl iodide. In addition to the normal rhodium(III) complexes more exceptional paramagnetic rhodium(II) compounds have been formed in these oxidation reactions. The electron spin resonance spectra of the paramagnetic complexes show a very large $\bar{\bar{g}}$-anisotropy. This anisotropy has been interpreted with a simple ligand field mod-

el (Chapter III).

Infrared intensity measurements have been done on complexes of rhodium and other group VIII metals with substituted acetylenes as ligands. A quantum-chemical treatment of symmetry-adapted orbitals has made it possible to separate with the aid of the measured intensities the different components of the metal-alkyne bond in these complexes (Chapter IV).

The various results showed an obvious influence of the coordination number of the metal on the bond between the metal and the organic molecule. This influence has been analysed by means of orbital correlations and has been supported by further literature data (Chapter V).

S A M E N V A T T I N G

Rhodiumcomplexen met fosfines als liganden zijn actieve katalysatoren voor vele organische reakties. De organische reagentia worden gedurende het katalytisch proces kortstondig aan het rhodium gebonden. Teneinde een organisch reagens te kunnen binden, moet het metaalcentrum onbezette koordinatieplaatsen hebben. Dit proefschrift beschrijft een synthetische studie van de stabilisatie van intermediairen in katalytische processen door het gebruik van een omvangrijk fosfine, en spektroskopische studies van diverse typen van intermediairen.

Door het gebruik van het omvangrijke tricyclohexylfosfine zijn voor het eerst rhodium(I)complexen met het lage koordinatiegetal 3 geisoleerd. Hierbij heeft de nieuwe verbinding $[RhF(cycloocteen)_2]_n$ goed dienst gedaan. Het bewijs voor de drie-koordinatie is met behulp van ^{31}P kern magnetische resonantie geleverd. De drie-gekoordineerde rhodium(I)verbindingen geven stabiele additieverbindingen met molekulaire stikstof en zuurstof, zowel als met een verscheidenheid van onverzadigde organische molekulen: CO, C_2H_4, acetylenen, CS_2, COS, RNCS, RNCO, RNCNR, SO_2 en PhNO. Sommige van deze verbindingen zijn bijzonder door de vier-omringing van het rhodium, andere door de nieuwe wijze waarop het organische ligand gebonden is (Hoofdstuk II).

De drie-gekoordineerde rhodium(I)verbindingen zijn geoxideerd door de additie van waterstof, halogeenzuren, halogenen en methyljodide. Daarbij zijn naast de gebruikelijke rhodium(III)verbindingen ook minder gewone paramagnetische rhodium(II)-complexen gevormd. De elektronen spin resonantie spektra van deze laatste vertonen een bijzonder grote anisotropie van de $\bar{\bar{g}}$-tensor. Deze anisotropie is ge-

interpreteerd met een ligandveldmodel (Hoofdstuk III).

Aan complexen van rhodium en andere groep VIII metalen met gesubstitueerde acetylenen zijn infraroodintensiteitsmetingen verricht. Een kwantumchemische behandeling van symmetrie-aangepaste orbitalen heeft het mogelijk gemaakt op basis van deze metingen de verschillende komponenten van de metaal-alkyn binding in deze complexen te scheiden (Hoofdstuk IV).

Uit de verschillende resultaten bleek een duidelijke invloed van het koordinatiegetal van het metaal op de binding tussen metaal en organisch molekuul te bestaan. Deze invloed is door middel van orbitaalkorrelaties geanalyseerd en met verdere literatuurgegevens gestaafd (Hoofdstuk V).

R E S U M E

Des complexes de coordination du rhodium avec des ligandes phosphines sont des catalyseurs actifs pour beaucoup de réactions de la chimie organique. Les réactifs organiques sont fixés passagèrement au rhodium durant le processus catalytique. Afin de pouvoir fixer le réactif organique, le centre métallique doit posséder des positions vacantes de coordination. Dans cette thèse il est décrit des études synthétiques de la stabilisation d'intermédiaires de processus catalytiques par l'utilisation d'une phosphine encombrante, et des études spectroscopiques de types divers d'intermédiaires.

En nous servant de la tricyclohexylphosphine, nous avons isolé pour la première fois des complexes dans lesquelles le rhodium(I) est trois fois coordonné. Pour ceci, le nouveau composé $[RhF(cyclo\text{-}octène)_2]_n$ a bien servi. La preuve du nombre de coordination de trois a été donné par les spectres de résonance magnétique des noyeaux ^{31}P. Les complexes du rhodium trois fois coordonné ont donné des composés stables d'addition avec l'azote moléculaire, avec l'oxygène moléculaire et avec un grand nombre de molécules organiques insaturées: CO, C_2H_4, acétylènes, CS_2, COS, RNCS, RNCO, RNCNR, SO_2 et PhNO. Quelques de ces complexes sont particuliers parce qu'ils contiennent le rhodium quatre fois coordonné, d'autres parce que la molécule organique est coordinée d'une façon nouvelle (Chapitre II).

Les complexes du rhodium(I) ont été oxidés par l'addition de l'hydrogène, des acides halogéniques, des halogènes et du CH_3I. Des complexes normaux du rhodium(III) et des complexes paramagnétiques du rhodium(II) d'une plus grande rareté ont été formés. Ces derniers montrent une anisotropie

très grande du tenseur magnétique électronique. Cette anisotropie a été interprètée avec la théorie du champ des ligandes (Chapitre III).

Les intensités de pics d'absorption dans les spectres d'infrarouge ont été mesurées d'une série de composés du rhodium et d'autres métaux du groupe VIII coordonnés par des acétylènes substitués. Par un traité de mécanique ondulatoire d'orbitales adaptées à la symétrie nous avons pu séparer grâce aux intensités mesurées les components différents de la liaison entre les métaux et les acétylènes (Chapitre IV).

Les résultats divers montraient une influence certaine du nombre de ligandes coordinés sur la liaison entre le métal el la molécule organique. Cette influence a été analysée par le moyen de corrélations d'orbitales et a été confirmée par des données tirées de la littérature (Chapitre V).

CURRICULUM VITAE

Henk van Gaal is geboren op 5 mei 1943 te Schaijk (NB). Hij heeft het Titus Brandsma Lyceum te Oss bezocht, alwaar hij in 1961 het diploma Gymnasium-β heeft behaald.

Van 1961 tot 1965 heeft hij een religieuze vorming genoten in de Societeit van Jezus, gedurende welke tijd hij het noviciaat volgde te Velp (NB) en filosofie studeerde in Heverlee (België) en Chantilly (Frankrijk). Wegens ziekte heeft hij deze opleiding in 1965 gestaakt.

Hij is in 1966 met de chemiestudie aan de Katholieke Universiteit van Nijmegen begonnen. Hij heeft op 7 juli 1969 cum laude candidaatsexamen S3 afgelegd en op 26 februari 1973 cum laude doctoraalexamen met hoofdvak Anorganische Chemie bij de hoogleraar J.J. Steggerda (als stage bij het Unilever Research Laboratorium te Vlaardingen, onder leiding van Dr. A. van der Ent), bijvak Molekuulspektroskopie bij de hoogleraar E. de Boer, onder leiding van Dr. J.G.M. van Rens en Dr. C.P. Keyzers, en capita wiskunde, quantumchemie, vaste stof chemie en instrumentele methoden. Gedurende zijn studie heeft hij een viertal studentassistentschappen vervuld en heeft hij deel uitgemaakt van de Onderwijscommissie van de vakgroep Chemie.

Sinds 1 maart 1973 is hij als wetenschappelijk medewerker verbonden aan de afdeling Algemene en Anorganische Chemie (hoofd: Prof.Dr.Ir. J.J. Steggerda) der Katholieke Universiteit te Nijmegen. Gedurende zijn promotiestudie heeft hij een kollege Organometaalchemie mede voorbereid en enige malen geassisteerd op het Anorganisch Chemisch Praktikum.

S T E L L I N G E N

1

Ongerijmdheden in de door James *et al.* en Van Vugt *et al.* gegeven interpretatie van E.S.R. spektra van ingevroren oplossingen van een rhodiumkomplex en molekulaire zuurstof worden opgeheven, indien de E.S.R. spektra niet aan één, als Rh(II)..O_2^- beschreven, deeltje, maar aan twee onafhankelijke deeltjes worden toegeschreven.

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2

Bij pogingen homogene rhodiumkatalysatoren (of katalysatorprecursors) chemisch te verankeren aan polymeerfosfines wordt vaak onvoldoende rekening gehouden met de labiliteit van de koordinatieband in verbindingen van rhodium(I).

3

Voor het oplossen van overgangsmetaalionen in epoxyharsen zijn veel alternatieven aantrekkelijker dan de macrocyclische polyetherkomplexen, voorgesteld door Spurr.

A.R. Spurr, in "Microprobe analysis as applied to cells and tissues", Ed. T. Hall, P. Echlin en R. Kaufmann (1974) p. 213.

4

Kilmantin *et al.* konkluderen ten onrechte, dat in aanwezigheid van IHP het verschil in Bohr effekt tussen hemoglobine en des(Arg*141*α, Tyr*140*α, Lys*139*α) hemoglobine overeenkomt met de bijdrage van Val*1*α tot het Bohr effekt.

J.V. Kilmantin, J.A. Hewitt en J.F. Wootton, J. Mol. Biol. 93, 203 (1975).

5

Omdat het door Rein *et al.* gegeven lineaire verband tussen molekuulgewicht en Mössbauerfraktie berust op een petitio principii, is de door hen genoemde onverwacht goede overeenstemming tussen theorie en experiment een artefact.

A.J. Rein en R. Herber, J. Chem. Phys. 63, 1021 (1975).

6

De huidige Krankzinnigenwet (en het wetsontwerp Bijzondere Opnemingen in Psychiatrische Ziekenhuizen) laat dwangmaatregelen toe tegenover personen, die mogelijk geestesziek zouden kunnen zijn, zonder dat tevens voldoende de rechten van deze personen tegenover onterecht of te lichtvaardig gebruik van deze wet en de daaruit voortvloeiende geestelijke en materiele onvrijheden beschreven worden. Onder meer verdient het aanbeveling, zolang de wet nog de mogelijkheden van in bewaring stelling en van rechterlijke machtiging tot opname biedt, de betrokken "psychiatrisch vervolgde" tenminste die rechten te geven, die een op strafrechtelijke gronden vervolgde heeft.

7

Dezelfde euforiserende werking van minor tranquilizers zoals Valium^{R}, welke voor de arts aanleiding is ze voor te schrijven, is bij de gebruiker vaak reden tot psychologische verslaving. De arts haalt met deze middelen dus het Paard van Troje binnen zijn veste.

8

Het is aanvechtbaar dat geesteszieken gedurende maanden of jaren aan geestdodend werk, als het maken van wasknijpers of het inzetten van rijwielspaken, gezet worden: ook de psychiatrische patient heeft recht op passende arbeid.

9

Le projet d'une route touristique à travers les dunes de Biville (Hague) doit être déconseillé, parce qu'une telle route n'améliorera pas l'accessibilité des habitations existantes, qu'elle aura une influence défavorable sur la commerce locale, et qu'elle sera une détérioration de la beauté du paysage.

10

Nederland verhardt.

11

De poriën in het papier van een stellingenblad zijn fijn genoeg om er muggen mee te ziften.

Nijmegen, 25 februari 1977 H.L.M. van Gaal